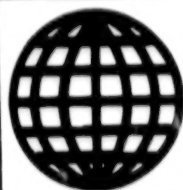


JPRS-UCH-92-009  
10 November 1992



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# ***JPRS Report***

# **Science & Technology**

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***Central Eurasia:  
Chemistry***

# Science & Technology

## CENTRAL EURASIA: Chemistry

JPRS-UCH-92-009

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**Computer Simulation of the Precipitation Titration of Multicomponent System**

927M0170A Moscow *ZHURNAL ANALITICHESKOY KHIMII* in Russian Vol 47 No 4, Apr 92 (manuscript received 20 Mar 91) pp 581-586

[Article by V.A. Kropotov, Simferopol State University; UDC 543.25]

[Abstract] Computer simulation of acid-base titration has been described in rather great detail. The procedures entailed in computer simulation of precipitation titration have received far less attention in the literature, however. In view of this fact, the author of this article has described a procedure for computer simulation of precipitation titration of multicomponent systems. The procedure is based on the following assumptions: the precipitates are in equilibrium with the solution, the formation of solid solutions and adsorption of ions on the surface of the solid phase are insignificant, the changes in the solubility product due to aging of the precipitates may be ignored, and the ionic strength of the solution is completely controlled by the background electrolyte. The proposed computer simulation procedure does not consider side complexing reactions. Such reactions may be easily taken into account for the practically important case of a constant ligand concentration. This is done by replacing the concentration constants of the precipitation reaction by conditional constants. Two approaches to using the proposed scheme for simulating precipitation titration are described. The first entails specifying the volume of titrant added and finding the respective equilibrium ion concentrations. The second approach entails calculating the volume of titrant that must be added to the mixture undergoing titration in order to reach the prespecified ion concentration characterizing the precipitation titration process. Each of the methods has its own particular pros and cons. The first approach is fully consistent with experimental conditions but requires special numerical methods to solve the required equations at each point of the precipitation titration. This method is convenient in cases where the increment of the change in titrant volume is constant. The second approach is preferred in cases where legs of the curve close to equivalence points or other selected points must be studied in detail (for example, when developing, selecting, or optimizing precipitation titration methods). The second approach may also be recommended for use with computer graphics when depicting a titration curve. References 10: 9 Russian, 1 Western.

**Estimating Different Components of the Systematic Error of a Quantitative Chemical Analysis of Real Specimens by Using a Combined Method of Doubling the Sample and Using Standard Additives**

927M0170B Moscow *ZHURNAL ANALITICHESKOY KHIMII* in Russian Vol 47 No 4, Apr 92 (manuscript received 7 Mar 91) pp 603-607

[Article by D.B. Gladilovich, St. Petersburg State University; UDC 543.062:389.14]

[Abstract] As a way of estimating the different components of the systematic error of a quantitative analysis of real specimens in the absence of standard specimens of a composition or certified mixtures, others have proposed a method that combines a scheme of doubling samples and standard additives. According to these authors, three series of measurements are taken simultaneously. The first or base series of measurements entails an analysis using some weighted portion of a sample. The weighted portion is doubled in the second series of measurements. Finally, some known quantity of the component being determined is added to the starting sample in the third series of measurements. The systematic error of a quantitative chemical analysis of some component of a real sample may, according to these authors, be determined from a linear model consisting of three equations. According to the author of the present model, the validity of the above method has been demonstrated adequately, and no concrete examples of its use are available. He has presented his own modification of the above method. The modification includes additional terms that give consideration to the effect of accompanying components. As an illustration of his new method of determining systematic error, he presents the results obtained during complexometric titration of solutions simultaneously containing scandium and yttrium. On the basis of his tests of the proposed systematic error determination method, he concludes that the new procedure may be used to detect only the presence of significant systematic errors that do not depend on the content of accompanying component. Although the new modification of the new technique of doubling a sample and adding standard additives does not entirely eliminate systematic errors, it does reduce their magnitude somewhat. Tables 2; references 5 (Russian).

**An Optoimmunosensor for Simultaneous Determination of Several Substances Based on a "Dying" Wave**

927M0170C Moscow *ZHURNAL ANALITICHESKOY KHIMII* in Russian Vol 47 No 4, Apr 92 (manuscript received 13 Mar 91) pp 613-622

[Article by P.Ya. Arenkov, N.F. Starodub, and V.A. Berezin, Molecular Biology and Genetics Institute, Ukraine Academy of Sciences, Kiev, and Dnepropetrovsk State University; UDC 577.18:577.15:541.543]

[Abstract] Optoimmunosensors based on the use of labeled components of an immunochemical reaction (i.e., an antibody) may be classified as being of one of two types, i.e., the transmission type and the type based on rapidly dying waves. The authors of the study reported herein worked to develop a new dying wave-based optoimmunosensor for simultaneous determination of several substances. Like other dying wave optoimmunosensors, the new optoimmunosensor described herein consists of a laser light source and fluorescence collection system that in turn consists of the following components: a lens, a dichroic mirror and

narrowband interference light filters, optical fiber with a sensitive coating, and a flowthrough cell to allow the specimen to be input for analysis. Antibodies are covalently immobilized on the surface of the core of the optical fiber (or optical rod), while fluorophore-labeled antigens [ $\text{Ag}^+$ ] are input through the flow-through cell surrounding the optical fiber. The  $\text{Ag}^+$ -Ab complexes formed result in an associated fluorescent signal and remote detection. The new optoimmunosensor has an optrode as its immunosensor. The optrode is made of quartz optical rods 60 mm long and 1.3 mm in diameter that have parallel ground and polished surfaces. The optrode's surface has been modified to immobilize antibodies. In order to form the maximum number of hydroxyl groups, the rods were immersed into hot acetone for 30 minutes and then subjected to hydration by immersing them in boiling water for 5 hours. This regimen can produce hydroxyl groups in a density as high as  $5 \times 10^{18} \text{ m}^{-2}$  or  $3 \mu\text{mol/m}^2$ . In order that oriented active groups will be produced on the optrodes' surfaces, they are treated in a 2% solution of monofunctional 4-aminobutyldimethylmethoxysilane in acetone for 40 minutes at  $60^\circ\text{C}$ . Next, the optrodes are rinsed in distilled water and dried for 40 minutes at  $100^\circ\text{C}$ . The optrodes' surfaces are modified further by immersing them for 40 minutes into a 2.5% solution of glutaric dialdehyde with a pH of 6.8 at room temperature. Finally, the optrodes are carefully rinsed in a  $5 \times 10^{-2} \text{ M}$  phosphate buffer solution with a pH of 7.2. To immobilize the antibodies, the modified optrodes are immersed for 1 hour at room temperature into a solution containing 500  $\mu\text{g/ml}$  of a 1:1 antibody to phenytoin or lidocaine solution in a phosphate buffer solution. The free functional groups of the dialdehyde are blocked by immersing them into yet another solution. Tests of the new optoimmunosensors established that they have minimum response times of 50 and 75 s in lidocaine and phenytoin, respectively, with concentration measurements in the range from 20 ng/ml to 20  $\mu\text{g/ml}$ . Further tests to determine the dependence of the immunosensor's response on the concentration of substances being determined with different measurement times were conducted by using phenytoin. The tests established that that portion of response giving the optoimmunosensor a sensitivity at the level of 100 ng/ml is achieved after 2 minutes. Tests to determine whether the new optoimmunosensors could be used repeatedly revealed that after 10 measurements their sensitivity decreases by nearly an order of magnitude and that the intensity of their maximum signal decreases by about 20%. The variance of the optoimmunosensor's signal did not exceed 3 to 8% from optrode to optrode. The new optoimmunosensors proved to be suitable for use in the simultaneous determination of lidocaine and phenytoin in a concurrent immunochemical chemical analysis with fluorescein thioisocyanate and R-phycoerythrin as labeling agents. The new optrodes were demonstrated to operate properly when stored in dry form at  $4^\circ\text{C}$  for up to 2 months. Figures 7, table 1; references 12: 4 Russian, 8 Western.

### The Use of Fusible Aromatic Compounds To Extract Platinum and Palladium Mercaptoquinolinates From Aqueous Solutions

927M0170D Moscow, ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 47 No 4, Apr 92 (manuscript received 19 Apr 91) pp 636-643

[Article by S.V. Mashkina, N.A. Ulakhovich, G.K. Budnikov, and A.P. Sturis, Kazan State University imeni V.I. Ulyanov-Lenin, UDC 543.42]

[Abstract] Research was done to develop a method of using fusible aromatic compounds to extract platinum and palladium mercaptoquinolinates from aqueous solutions. As extractive reagents, the researchers used sodium salts of 8-mercaptoquinolines containing the following substituents: 2- $\text{CH}_3\text{S}$ -, 2- $\text{C}_6\text{H}_5\text{S}$ -, 4- $\text{CH}_3\text{S}$ -, 4- $\text{CH}_6\text{H}_5\text{S}$ -, 5- $\text{CH}_3\text{S}$ -, 5- $\text{CH}_6\text{H}_5\text{S}$ -, 7- $\text{C}_6\text{H}_5\text{O}$ -, and 7- $\text{C}_6\text{H}_5\text{S}$ -.  $\text{Pd(II)}$  and  $\text{Pt(IV)}$  solutions were prepared from chemically pure  $\text{PdCl}_2$  and  $\text{K}_2\text{PtCl}_6$ , and their concentrations were refined by complexometric titration. Voltammetry (with a PU-1 polarograph) and spectrophotometry (with an SF-26 spectrophotometer) techniques were used to study the distribution of palladium and platinum mercaptoquinolate between the aqueous phase and melt of the organic extractive solvent. A twofold excess of reagent was found to be necessary for quantitative extraction of palladium to a melt. In the case of platinum (IV), at least a sixfold excess of sodium mercaptoquinolate was required. Attempts to use paraffin to extract the study chelates proved unsuccessful (the degree of extraction did not exceed 10% regardless of the reagent used). The replacement of alkyl substituents by aromatic ones significantly improved the mercaptoquinolines' extraction properties. It was hypothesized that the resultant increase in hydrophobicity likely results in a noticeable increase in their solubility in the organic phase. The acidity of the aqueous phase was found to have a significant effect on the complexing equilibrium (i.e., on the chemism of the extraction process) by changing the form in which the reagent and metal ions exist. The range of aqueous phase acidity levels resulting in quantitative extraction was found to be broader in the case of palladium than in the case of platinum regardless of the extractive solvent used. The maximum degree of extraction was achieved by using *n*-dichlorobenzene as an extractive solvent (dibenzyl resulted in the minimum degree of extraction [ $R = 92\%$ ]). 2-Methylnaphthalene and naphthalene also proved to be highly effective as extractive solvents. The studies established that at solution temperatures of 35 to  $38^\circ$ , platinum is not transferred to 2-methylnaphthalene for more than 30 minutes, whereas palladium is extracted in 5 to 7 minutes. This difference in extraction times creates the possibility of separating palladium from platinum. The various factors affecting the degree of extraction were discussed. Under optimal conditions, a 100- to 120-fold concentration of the study metals is possible. Figures 5, tables 2; references 22: 15 Russian, 7 Western.



**X-Ray Microanalysis of Gas-Saturated Layers  
Formed During the Oxidation of Titanium**

927M0170E Moscow ZHURNAL ANALITICHESKOY  
KHIMII in Russian Vol 47 No 4, Apr 92 (manuscript  
received 13 Nov 90) pp 731-736

[Article by S.N. Petrov and R.A. Zvinchuk, Prometey  
Central Scientific Research Institute of Building Mate-  
rials, St. Petersburg, and St. Petersburg State University;  
UDC 543.422.8]

[Abstract] A method of plotting the concentration profile of oxygen in gas-saturated layers of titanium and its alloys was developed. A JCXA-733 x-ray microanalyzer (Jeol, Japan) and LSI-11/23 computer were used in the studies. All of the measurements were made on specimens of iodide and commercial-grade titanium, titanium-aluminum alloys, and the titanium alloy VT5-1. The specimens were oxidized in air at temperatures of 800 to 900°C for 5 to 180 minutes. Polycrystalline specimens with a grain size of 3 to 8  $\mu\text{m}$  were used. An  $\text{Fe}_{0.92}\text{O}$  synthetic wustite crystal that contained 20.1% oxygen and possessed good conduction was used as a comparison oxygen-containing specimen. The experiments performed revealed that the determination of oxygen in titanium by the method of x-ray microanalysis

is fraught with a number of problems. First, the exceedingly high coefficient of the absorption of  $\text{OK}_{\alpha}$  radiation in the matrix ( $\mu/\rho = 22,140 \text{ cm}^2/\text{g}$ ) requires that absorption in the specimen be taken into consideration as precisely as possible. Second, the titanium surface is always covered with a natural oxide film. The oxygen present in this film distorts analysis results to varying degrees depending on the accelerating voltage used: The distortion may be equivalent to a content of several percentage points of oxygen in the metal. Special corrections are therefore required to reduce this distorting effect of the oxide film. The authors have derived an expression for determining the appropriate atomic number and absorption corrections. Concentration profiles plotted on the basis of x-ray microanalysis and calculations incorporating the appropriate corrections confirmed that x-ray microanalysis is indeed a feasible method for use in studying gas-saturated layers in metals. The limiting dimensions of the area of a specimen that may be thus studied are 2  $\mu\text{m}$  along the surface and 0.3  $\mu\text{m}$  into the depth of the specimen. The proposed method has a detection threshold at the level of 0.4% (mass) provided that the thickness of the oxide film present on the specimen is calculated in advance and taken into consideration by means of the appropriate corrections. Figures 4; references 9: 7 Russian, 2 Western.



**Effect of Electron Structure on Hydrogenation of 4-Ter- butylphenol Over Metal Catalysts**

927M0167A Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 5, May 92 (manuscript received 4 Jun 91) pp 1033-1037

[Article by A. M. Pak and O. I. Kartonozhkina, Organic Catalysis and Electrochemistry Institute imeni D. V. Sokolskiy; UDC 541.128.3:530.145:541.27:542.941.7:547.562.1:546.3-44]

[Abstract] Various mechanisms have been proposed for the hydrogenation of phenol. Data collected in the case of a Pd-on- alumina catalyst suggest that hydrogen atoms are adsorbed during the first four stages of sequential addition to the phenol molecule. Two hydrogen atoms are then simultaneously added to the newly formed cyclohexane molecule. Using RMX and CNDO/2 methods, calculation of the limiting states of the phenol molecule during reactions with proton donors and acceptors indicate that redistribution of electron density must lead to a change in energy of the intermolecular bonds. In the present work a quantum chemical analysis of probable 4-ter-butylphenol hydrogenation mechanisms was performed using INDO approximation. The effect of adsorption mode on disruption of aromatization was also examined. References 11: 7 Russian, 4 Western.

**IR-Spectra of Catalysts and Adsorbed Molecules. Report 39. Acid and Catalytic Properties of Pentacils, Modified with Platinum, Chromium, and Zinc**

927M0167B Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 5, May 92 (manuscript received 16 May 91, after revision 22 Jul 91) pp 1038-1042

[Article by L. I. Lafer, Zh. L. Dykh, T. V. Vasina, A. V. Preobrazhenskiy, O. V. Brazin (deceased), V. I. Yakerson, Organic Chemistry Institute imeni N. D. Zelinskiy, Moscow; UDC 541.128.34:542.97:543.422.4:547.313.3]

[Abstract] Modification of zeolites with metals or metal oxides alters their physical chemical properties making it possible to prepare active and selective catalysts for conversion of low molecular alkanes into aromatic hydrocarbons. In the present work a study was made of the acidity of a number of modified (Pt, Pt-Cr, and Pt-Cr-Zn) pentacil-containing catalysts and their catalytic properties in the aromatization of C<sub>1</sub>-C<sub>3</sub> alkanes. It was demonstrated that introduction of platinum to pentacil results in a 2-fold increase in the concentration of L-sites with no change in concentration of B-sites. In Pt-Cr catalysts, the L-site concentration passes through a maximum at 0.72 percent Cr, while the number of hydroxyl groups in the B-site falls. In samples promoted simultaneously with Pt, Cr, and Zn, the concentration of B-sites falls and that of the L-sites increases. Under conditions of lower alkane aromatization, the concentration of B-sites on the catalysts falls while that of the L-sites increases. Introduction of platinum to pentacil raises the

aromatization activity in respect to methane; supplemental introduction of chromium and zinc raises the aromatic hydrocarbon yield from both ethane and propane. Figure 1; references 10: 6 Russian, 4 Western. an

**Mechanism of Activation and Catalysis with Chelate Eu(fod)<sub>3</sub> of Chemiluminescence During Thermal Decomposition of Adamantylideneadamantane-1,2-dioxethane**

927M0167C Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 5, May 92 (manuscript received 16 Apr 91, after revision 5 Dec 91) pp 1056-1063

[Article by A. I. Voloshin, G. L. Sharipov, V. P. Kazakov, and G.A. Tolstikov, Organic Chemistry Institute, Ufa; UDC 535.379:535.373.2:547.124.541.147.2]

[Abstract] Chelate complexes of lanthanides are effective energy acceptors of singlet- and triplet-excited ketones and are also capable of activating chemiluminescence in dioxyethanes formed during decomposition of excited carbonyl compounds. Coordination- unsaturated lanthanide chelates, such as those utilized in NMR- spectroscopy as paramagnetic shifting reagents, intensify dioxyethanes chemiluminescence while catalyzing their decomposition. Owing to complex formation between chelates and ketones and dioxyethanes, the mechanism of chemiluminescence and decomposition kinetics of the latter becomes very complex in comparison to non-catalyzed decomposition. In the present work a study was made of the catalysis of decomposition and chemiluminescence of adamantylideneadamantane-1,2-dioxethane in the presence of Eu(fod)<sub>3</sub>. It was demonstrated that the chemiluminescence occurring during thermal decomposition of adamantylideneadamantane-1,2-dioxyethane in the presence of Eu(fod)<sub>3</sub>, complex formation processes of the chelate with both the dioxyethane and adamantanone, a decomposition product of dioxyethane, have a significant effect. Stability constants were determined for both complexes and it was demonstrated that Eu(fod)<sub>3</sub> catalyzes and activates chemiluminescent decomposition of adamantylideneadamantane-1,2- dioxyethane. Figures 5; references 15: 9 Russian, 6 Western.

**Stoichiometric and Catalytic Methods for Asymmetric Synthesis of Non-protein α- and β-Amino Acids Through Coordination Compounds of Transition Metals**

927M0167E Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 5, May 92 (manuscript received 2 Dec 91) pp 1106-1127

[Article by Yu. N. Belokon, Elementoorganic Compounds Institute, Moscow; UDC 541.63:542.91:547.466'161]

[Abstract] The production of proteinic optically pure amino acids is a rapidly expanding area of modern

industry. Synthesis methods are well developed, especially microbiological ones which provide optically pure products directly. Optically pure amino acids are currently inexpensive; some have a wholesale price below five dollars per kilogram. Synthesis methods for optically pure non-proteinic amino acids, however, have attracted the attention of researchers recently owing to the fact that many parameters of the physiological activity of the latter may be altered by exchanging proteinic amino acids with non-proteinic amino acids. Also, many antibiotics consist of peptides which contain non-proteinic amino acids of varied structure, and therefore chemical synthesis of such modified peptides and antibiotics requires development of synthesis methods for unusual amino acids. Unfortunately, enzymatic and microbiological methods are unsuitable, while traditional chemical methods give racemic products which must be split into enantiomers, thereby raising costs to 50-300 dollars per gram. While some outstanding results have been reported, proposed methods for synthesis of the above are limited to only a few grams of amino acids. In the present work an original method was developed for the asymmetric synthesis of proteinic and non-proteinic amino acids employing a single source - glycine, and a single chiral reagent which may be regenerated, i.e. chiral complex of glycine with transition metals. Complexes formed from Ni(II) and Cu(II) ions and the glycine-based Schiff bases,  $\alpha$ -alanine and  $\beta$ -alanine with (S)-[N-(N-benzylpropyl)-amino]benzophenone, engage in various electrophilic and nucleophilic reactions to form diastereoisomeric complexes which decompose into proteinic and non-proteinic L-amino acids at high yield and high (70-80 percent) optical purity. Optically pure amino acids may be obtained from the diastereoisomerically pure complexes after recrystallization. References 10: 1 Russian, 9 Western.

#### Synthesis of Naphthyridines and Phenanthrolines Using Transition and Rare Earth Metal Catalysts

927M0167F Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 5, May 92 (manuscript received 14 Jun 91) pp 1139-1148

[Article by U. M. Dzhemilev, F. A. Selimov, R. A. Khusnutdinov, A. A. Fatykhov, Ye. I. Andreykov, and G. A. Obanin, Eastern Coal Chemical Institute (AU), Sverdlovsk; UDC 541.128:546.65:542.953:547.551:547.281:547.571:547.831

[Abstract] Current practice for the synthesis of phenanthrolines and naphthyridines uses a classic method based on the condensation of aminoquinolines with glycerine or acrolein. However, this method is good for only the most simple representatives of the above heterocyclics and cannot be used to synthesize their alkyl- and aryl-substituted derivatives with satisfactory yields. Liquid phase catalytic condensation of aromatic amines with aldehydes into corresponding quinolines opens up new possibilities in the synthesis of these heterocyclics. In the present work it was demonstrated that liquid phase condensation of 3-, 4-, and 8-aminoquinolines with

aliphatic and aromatic aldehydes, catalyzed with transition metal and rare earth metal metals is an effective method to synthesize substituted 1,7- and 1,6-naphthyridines and 1,10-phenanthrolines. References 5: 2 Russian, 3 Western.

#### Ruthenium Catalysts for Liquid Phase Hydrocracking of n-Alkanes

927M0167I Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 5, May 92 (manuscript received 2 No 91, after revision 6 Dec 91) pp 1211-1213

[Article by I. S. Akhrem, S. Z. Bernadyuk, and M. Ye. Voipin, Elementoorganic Compounds Institute, Moscow; UDC 542.925.7:547.259.6]

[Abstract] It was previously demonstrated that by using a Ziegler type catalyst system and low ligand clusters of transition metals (MLK), it is possible to synthesize active catalysts for liquid phase hydrocracking of paraffins. Carbonyl and carbonyl hydride complexes of rhenium in conjunction with Al-organic compounds are catalysts for hydrocracking of alkanes and cycloalkanes at 150-180° C and 5 MPa hydrogen pressure. One mole of rhenium complex catalyzes the conversion of 100 moles of hydrocarbon in 3-15 hours. All available data suggests that the catalysts formed in these systems consist of metal-organic hydrides of rhenium. Another route for synthesis of hydrocracking catalysts is homogeneous reduction of transition metal compounds under conditions excluding deactivation of the formed MLK. This made it possible to synthesize Os-MLK having 7-16 angstroms particle size, highly active in hydrocracking alkanes and other reactions. In the present work catalysts for liquid phase hydrocracking of n-alkanes exceeding Ru-black in activity were prepared by decomposing in alkanes  $Ru_3(CO)_{12}$ ,  $Ru_3(CO)_{12} + iso-Bu_2AlH$  at 180-200° C and 5 MPa hydrogen pressure and (benzene)(cyclohexadiene-1,3)ruthenium at 20° C and 0.1 MPa hydrogen pressure. References 6: 3 Russian, 3 Western.

#### Possibility of Isobutane Dehydrogenation with Carbon Dioxide over Manganese-Containing Catalysts

927M0167J Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 5, May 92 (manuscript received 29 Dec 91) pp 1230-1231

[Article by S. R. Mirzabekova, A. Kh. Mamedov, and O. V. Krylov, Petrochemical Processing Institute imeni Yu. G. Mamedaliyev, Baku; Chemical Physics Institute imeni N. N. Semenov, Moscow; UDC 547.211:622:763:542.962]

[Abstract] It was previously reported that it is possible to use  $CO_2$  as an oxidizing agent in heterogeneous catalytic processes. In the present work it was demonstrated that selective dehydrogenation of isobutane is possible with  $CO_2$ . Results on the conversion of isobutane in the

presence of  $\text{CO}_2$  on manganese-containing catalysts are presented. In contrast to alumina-platina catalysts, the conversion proceeds without accumulation of coke at  $750^\circ\text{C}$  and 3600 hourly space velocity. Isobutylene yield comprises 35 percent (based on isobutane throughput) with 65 percent isobutane conversion. The isobutylene formation follows a redox scheme. Isobutane destruction as a side reaction is the result of thermal splitting of the C-C bond. References 3: 2 Russian, 1 Western.

#### Forming an Ordered Packing of Sphere-Shaped Catalyst in a Tubular Reactor

927M0168B Moscow *TEORETICHESKIYE OSNOVY KHIMICHESKOY TEKHNologii* in Russian Vol 26 No 3, May-Jun 92 (manuscript received 20 Nov 89) pp 383-389

[Article by R.Z. Adinberg; UDC 66.023]

[Abstract] A principle for designing multilayer cylindrical structures that may in turn be used as a basis for forming ordered packings of spheres in tubes was proposed. Of the possible ways of closing a plane layer into a cylindrical surface, the author chose the one according to which some of the straight lines of the two-dimensional net are transformed into a circle while others are transformed into a spiral. This option was selected because it simplifies the transition from single- to multilayered structures. The number of spirals equals the number of nodes lying on the cylinder's circumference, and the number of cylinder starts  $n$  equals 3 or more. The densest packing is achieved when  $n$  equals 3, 4, or 5. Single-layer structures examined are examined first. They are shown to be self-ordering. The case of a three-start structure is shown to occupy an intermediate position between single- and multilayer structures. The analysis was then used as the basis for formulating an experiment on the self-ordered formation of a multilayer packing of spheres in a tube. A glass tube with an inner diameter of 50.3 mm and length of  $D = 600$  mm was used along with polished steel spheres with a diameter of  $d = 6$  mm ( $n = 8, 4$ ). A matrix in the form of a metal disk with pointed annular grooves was placed in the bottom end of the tubes. The grooves were designed so that distinct monolayers with 1, 12, and 23 spiral starts could be established on them. The experiment confirmed that it is indeed possible to achieve a dense multilayer cylindrical structure in a tube thanks to the mechanism of the self-ordering that is manifested in the formation of a multilayer structure. Additional research on the hydrodynamic and heat-and-mass transfer characteristics of multilayer packings of spheres, a process to form spherical catalysts meeting stringent requirements regarding sphericity and the variance of granule sizes, and the creation of loading devices capable of guaranteeing a specified mass flow rate of granular material is needed before ordered cylindrical structures can be implemented in commercial multitube chemical reactors. Figures 6; references 5 (Russian).

#### Oxidation of Ethyl Alcohol over Sn-Mo-Oxide Catalyst

927M0175G Moscow *ZHURNAL FIZICHESKOY KHIMII* in Russian Vol 66, No 4, Apr 92 (manuscript received 19 Feb 91) pp 959-963

[Article by G. O. Tuarshva, V. L. Bagiyev, and K. Yu. Adzhamov, Petroleum and Chemistry Institute, Baku; UDC 66.097.13:541.124]

[Abstract] One of the basic industrial methods for preparing acetic acid consists of two-stage oxidation of ethanol through acetaldehyde. Many references appeared in recent years on a single stage method of gas phase oxidation of ethanol to acetic acid over silver and oxide catalysts. In contrast to oxidation over silver catalysts, the formation of ethanol oxidation products over oxide catalysts has not been well studied. In the present work a study was made of the various conversions of ethanol over Sn-Mo-oxide catalysts. It was demonstrated that the basic reaction products consist of acetaldehyde, acetic acid, ethylene, and carbon monoxide. Study of the effect of water vapor on the process with deuterium revealed that water acts directly in the formation of acetic acid. An overall reaction for conversion of ethanol into acetic acid is presented. Figures 4; references 7 (Russian).

#### The Catalytic Carbonylation of Nitrobenzene by Carbon Oxide in the Presence of Organometallic Compounds of Transition Metals and Sulfur Derivatives

927M0178F St. Petersburg *ZHURNAL OBSHCHEY KHIMII* in Russian Vol 61 (123) No 12, Dec 91 (manuscript received 6 May 91) pp 2776-2777

[Article by A.O. Kolmakov, V.P. Bystrov, Ye.N. Tarasov, Yu.A. Aleksandrov, and Yu.I. Dergunov, Chemistry Scientific Research Institute, Nizhegorod State University imeni N.I. Lobachevskiy; UDC 546.262.331:547.546:541.128]

[Abstract] The catalytic carbonylation of nitrobenzene by carbon oxide in the presence of organometallic compounds of transition metals and sulfur derivatives was examined. Specifically, they established that a binary catalytic system consisting of bis-cyclopentadienyl metal dihalides with the composition  $\text{Cp}_2\text{MX}_2$  (where  $\text{M} = \text{V}$  (III),  $\text{Mo}$  (IV), or  $\text{W}$  (V) and  $\text{X} = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ ) and alkaline metal polysulfides with the composition  $\text{M}'_2\text{S}_n$  (where  $\text{M}' = \text{Na}$  (VI) or  $\text{K}$  (VII) and  $n = 1, 2, 3, 4$ , or  $5$ ) catalyzes the carbonylation of nitrobenzene by carbon oxide in hydroxyl-containing media to carbamates and amines with a close-to-quantitative yield of target products. Vanadium (III) proved to be the most active of the organometallic compounds studied, while the polysulfides proved to be the most active of the sulfur-containing compounds. The optimal conditions for synthesizing carbamate and aniline in the presence of sulfur-vanadium catalytic systems were found to be as follows: molar ratio of reagents (VI):(III):(I) = 1:0.01-0.5:5-20; reaction time, 5 to 30 minutes; CO pressure, 60 atm or



higher; temperature, 165 to 185°C; and medium, alcohol in the case of methyl-N-phenylcarbamate and alcohol-water in the case of aniline. In the absence of vanadium derivatives, the yield of target products, i.e., methyl-N-phenylcarbamate or aniline, was found to not exceed 15 to 30%. References 2 (Russian).

**Vanadium (V) Peroxy Complexes Catalyzing Hydrogen Peroxide Conversions in Trifluoroacetic Acid**

927M0188A Moscow KOORDINATSIONNAYA KHIMIYA in Russian Vol 18 No 1, Jan 92 (manuscript received 14 Aug 91) pp 3-25

[Article by A. Ye. Gekhman, N. I. Moiseyeva, I. I. Moiseyev, Institute of General and Inorganic Chemistry imeni N. S. Kurnakov, USSR Academy of Sciences; Institute of Chemical Physics imeni N. N. Semenov, USSR Academy of Sciences; UDC 541.128:542.92:546.215:545.214]

[Abstract] Experimental results obtained by the authors and literature data were reported covering the effect of the reaction medium on peroxide breakdown process, and on the reactivity of intermediate complexes in respect to the organic substrates. It was observed that vanadium (V) complexes catalyze effectively the breakdown of hydrogen peroxide in trifluoroacetic acid forming up to 15% of ozone and leading to decarboxylation of the acid. Ozone formation results from a two electron internal oxidation of  $O_3^{2-}$  by an  $O_2^{2-}$  group. The active complexes forming in the system  $H_2O_2$ -V(V)- $CF_3COOH$  are capable of hydroxylating cyclohexane under soft conditions with high selectivity; they can also oxidize arenes, perfluoro-arenes, perfluoro-olefines, etc. In this system, in contrast to other hydroperoxide oxidation systems, a transfer of  $O_2$  from the active intermediate reagents to the double bond of the unsaturated substrate takes place. The active complex appears to be an electrophilic agent with no localized charge on oxygen atoms. The most unique property of  $H_2O_2$ -V(V)- $CF_3COOH$  is that, in the series: cyclohexane-arenes-perfluoro-octene-1-internal perfluoro-olefines, each preceding member of the series can prevent the consumption of all the following members of the series during a combined oxidation, probably because these later oxidations occur at a much lower rate. It was shown that hydrogen peroxide, as well as the peroxytrifluoroacetic acid participate in forming these complexes. A model was proposed for these reactions which included an internal rearrangement of two peroxy ligands into a  $(O_3^{2-})$  grouping. Tables 6; figures 6; references 36: 22 Russian (5 by Western authors), 14 Western (1 by Russian authors).

**Effect of Disintegrator Treatment of Metal-Like Catalysts on Specific Reaction Rate of Methane Oxidative Conversion**

927M0191A Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 58, No 5, May 92 (manuscript received 5 Apr 91) pp 377-380

[Article by L. N. Rayevskaya, B. I. Kolotysha, F. G. Pavlovskiy, N. I. Ilchenko, and B. I. Kipnis, Physical Chemistry Institute, Kiev; UDC 541.128]

[Abstract] Direct conversion of methane to ethylene, a key compound in organic synthesis, is an urgent goal. If the process is conducted in the presence of a metal-like catalyst, e.g. transition metal boride, silicide, or nitride, the methane dimerizes to form  $C_2$  and  $C_3$  hydrocarbons with extensive oxidation. In a previous work it was demonstrated that the specific rate of overall methane conversion decreases hyperbolically with increasing specific surface of the above catalyst. In this work specific surface was altered by varying the chemical composition of the catalyst. In this case the process could be affected by two factors, the chemical nature of the catalyst, or its specific surface. In the present work it was demonstrated that the above relationship still holds even after altering the specific surface of the catalyst by grinding in a laboratory disintegrator. The process has a heterogeneous-homogeneous mechanism. Figure 1; references 8: 4 Russian, 4 Western.

**Effect of Preparation Conditions of Zeolite Ni/H-ZSM on Catalytic Properties of  $CO_2$  Hydrogenation Reaction**

927M0191B Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 58, No 5, May 92 (manuscript received 27 Mar 91) pp 382-386

[Article by N. P. Samchenko, I. S. Alcheyev, and Z. M. Zdornaya, Physical Chemistry Institute, Kiev; UDC 541.128+542.941.73]

[Abstract] An important feature of pentacil-type catalysts is their capability to catalyze the conversion of low molecular weight paraffins into aromatic hydrocarbons and gasoline fraction hydrocarbons. Introducing Group VIII metals into these catalysts makes it possible to obtain polyfunctional catalysts. It has been observed that zeolite Ni/H-ZSM displays a high hydroisomerizing activity in the conversion of benzene into methyl cyclopentane. Evidently, the activity of these catalysts is due to the proximity of hydrogenating and isomerizing sites, resulting in the unencumbered migration of an intermediate product and its eventual conversion. In the present work a study was made of the capability of zeolite Ni/H-ZSM to accelerate hydrocondensation during hydrogenation of  $CO_2$ . It was demonstrated that the bifunctional properties of a nickel-zeolite system, i.e. its hydrocondensation capability in  $CO_2$  hydrogenation reactions, is manifested whenever metallic or Brønsted acid sites are near. If the distance between them is increased due to the high reactivity of intermediate surface complexes ( $HCOOH$ ), hydrogenation to methane takes place. References 7: 6 Russian, 2 Western.

**Rules Governing Active Surface Formation in Oxides of Vanadium-Containing Systems for Hydrocarbon Dehydrogenation Reactions in Presence of Hydrogen Acceptors. Report 4. Catalytic and Physical-Chemical Properties of Vanadium-Zirconium and Vanadium-Titanium Catalysts for Reaction of Oxidative Dehydrogenation of Ethyl Benzene in Presence of Nitrobenzene**

927M0193A Moscow IZVESTIYA AKADEMII NAUK ROSSIYSKOY AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 3, Mar 92 (manuscript received 11 Jan 91) pp 557-561

[Article by I. P. Belomestnykh, Ye. A. Skrgan, N. N. Rozhdestvenskaya, and G. V. Isagulyants, Organic Chemistry Institute imeni N. D. Zelinskiy, Moscow; UDC 536.51:537.531:541.128:541.183:546.881-31:542.941.8:543.422.6:546.824-31:546.831.4]

[Abstract] In order to carry out oxidative dehydrogenation over vanadium-containing oxide catalysts it is necessary to have active sites consisting of both oxidized and reduced vanadium ions situated preferably in octahedral coordination with a nearby oxygen atom. The properties of vanadium-magnesium and vanadium-aluminum catalysts depend on the degree of vanadium ion aggregation on the surface. In the present work a study was made of the catalytic and physical-chemical properties of vanadium-zirconium and vanadium-titanium systems in oxidative dehydrogenation of ethyl benzene in the presence of nitrobenzene. Conversion to styrene did not exceed 10 percent, and that of aniline - 60 percent. Study of the physical-chemical properties of the catalysts by electron spectroscopy, X-ray and differential thermal gravimetric analysis revealed the presence of three different vanadium ions, the proportions of which

varied with composition and concentration of the initial vanadium compound, the nature of the carrier, and the heat treatment conditions. References 10: 9 Russian, 1 Western.

**Evaluation of Catalyst Activity and Reactivity of Sulfur-Organic Compounds**

927M0193B Moscow IZVESTIYA AKADEMII NAUK ROSSIYSKOY AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 3, Mar 92 (manuscript received 4 Jan 91) pp 562-564

[Article by S. R. Ivanova, N. V. Tolmacheva, N. K. Lyapina, K. S. Minsker, and G. A. Tolstikov, Chemistry Institute, Ufa; UDC 542.973:655.63:542.924.4]

[Abstract] Halides of certain Group III-V metals are active as catalysts in the hydrogenolysis of sulfur-organic compounds. Owing to their strong acidity, these catalysts also initiate such side processes as polyaromatization and polymerization resulting in resin formation and catalyst deactivation. Catalysts prepared from complexes of  $AlCl_3$  with alkali metal chlorides are more moderate than the above in destruction of polyolefins, heavy and light crude oil fractions, while still retaining sulfur-purging properties. In the present work a study was made of the kinetics of hydrogenolysis of various classes of sulfur-organic compounds in the presence of Li-, Na-, and  $KAlCl_4$  catalysts. Reactions were conducted at 100-250° without hydrogen feed but in the presence of hydrocarbons fulfilling the function of hydride ion donor, required to form  $H_2S$ . Based on the reaction rate constants for hydrogenolysis at the C-S bond, a set of catalyst activities and optimum reaction conditions for each catalyst were determined. References 5 (Russian).



### Theory of Colloidal Aggregation

927M0190A Moscow KOLLOIDNYY ZHURNAL  
in Russian Vol 54, No 3, May-Jun 92 (manuscript  
received 9 Jan 92 pp 57-64)

[Article by A. Yu. Zubarev, Ural State University imeni  
A. M. Gorky, Yekaterinburg; UDC 541.18.04:536.423]

[Abstract] Colloidal aggregation commences with the unification of individual particles (monomers) into doublets, triplets, etc. to be followed by large aggregates containing very many particles. The first stage is normally analyzed on the basis of the DLFO theory, and general methods of the theory of first order phase transition are used to describe the evolution of large droplet-like aggregates. However, recent theoretical and experimental research demonstrated that large colloidal aggregates frequently have a fractal structure. Since the particle concentration in the fractal changes on passing from the center to the periphery, a similar cluster is not in a state of internal equilibrium and the probability of its genesis may not be described by methods of the equilibrium theory of fluctuation, as in the classic theory of first order phase transition. Therefore, standard methods of studying lamination kinetics of systems with low and high phase concentrations are generally inadequate for processes taking place in colloidal solutions. In the present work, a mathematical model of the growth of fractal colloidal aggregates is presented. Calculations, based on this model, show that the growth rate of fractal clusters may often exceed that of uniform aggregates, and therefore the classic theory of first order phase transition is inadequate for the process of formation and growth of colloidal aggregates. Figure 1; references 10 (Russian).

### Placing Liquid Films on Fine Cylindrical Filament

927M0190B Moscow KOLLOIDNYY ZHURNAL  
in Russian Vol 54, No 3, May-Jun 92 (manuscript  
received 30 Sep 91) pp 65-72

[Article by V. I. Ivanov, D. Kiri, Zh. M. du Megluc, and  
V. M. Starov, Food Industry Technological Institute,  
Moscow; College de France, Paris; UDC 541.1.18.04:  
536.423]

[Abstract] The problem of applying a liquid film on to a moving substrate is frequently encountered in technological processes. While much theoretical and experimental research has been done on this problem, the effect of disjoining pressure been ignored. In the present work a study was made of the application of films on to a moving, thin filament. An equation for film profile which takes into account disjoining pressure in the absence of gravity was developed, and a formula describing film thickness as a function of the velocity of the moving filament was derived. Experimental data agrees well with theoretical considerations. Figures 4; references 8: 4 Russian, 4 Western.

### Computing Electrical Conductivity of Polymeric Compositions with Polydispersed Fillers

927M0190C Moscow KOLLOIDNYY ZHURNAL  
in Russian Vol 54, No 3, May-Jun 92 (manuscript  
received 7 May 91) pp 73-75

[Article by G. B. Kozlov, V. A. Valtsifer, and B. A. Pogorelov, Physical Chemistry Institute, Moscow; Technical Chemistry Institute, Perm; UDC  
668.395.678.046.32: 537.311.4:541.5]

[Abstract] Much research has been published on the electrical conductivity of polymeric compositions containing various metallic powders or carbon-containing materials, and a method was developed for predicting the conductivity of these materials filled when with mono-spherical particles as a function of the concentration and properties of the components. In the present work a method for computing the conductivity of conductive polymeric materials having polydispersed fillers is presented. A model in which ordered filler chains are set up parallel to the direction of the current, and paired contact particles serve as structural elements, was chosen. Resistance of paired contacts was computed by a method based on the dominant effect of the shrinkage stresses formed during binder hardening. Formulas are presented for computing the forces and resistance of paired contacts which take into account polydispersed fillers. An algorithm was also developed for computing the conductivity of electrically conductive polymeric compositions which takes into account various types of paired contacts as well as their series and parallel contacts. References 7 (Russian).

### Role of Surface Tension Anisotropy in Liquid Crystals in Molecular Orientation on Solid Substrates

927M0190D Moscow KOLLOIDNYY ZHURNAL  
in Russian Vol 54, No 3, May-Jun 92 (manuscript  
received 18 Jan 91) pp 110-118

[Article by V. N. Matveyenko and Ye. A. Kirsanov,  
Moscow State University imeni M. V. Lomonosov;  
UDC 532.612]

[Abstract] The development of durable liquid crystal devices has drawn much interest to the problem of liquid crystal molecule orientation on substrates. Specially treated glass or quartz plates, often coated with clear electrically conductive coatings ( $\text{SnO}_2$ ,  $\text{In}_2\text{O}_3$ ) results in perpendicular, parallel, or inclined orientation of elongated liquid crystal molecules to the surface of the substrate. In the present work a critical analysis is presented on current colloidal chemical theories of orientation of liquid crystals on solid surfaces. Methods are presented for computing orientation of nematic liquid crystals on substrates and the anisotropy of interfacial energy. A classification of substrate-liquid crystal molecule systems which takes into account both dispersed and polar components is presented. Figures 3; references 17: 6 Russian, 11 Western.

**The Effect of Eddy Zones on the Intensity of Processes of Dust Separation and Combustion**

927M0168A Moscow *TEORETICHESKIYE OSNOVY KHIMICHESKOY TEKHNologii* in Russian Vol 26 No 3, May-Jun 92 (manuscript received 28 Jan 91) pp 347-353

[Article by M.P. Sharygin, Kazakh Chemical Technology Institute, Chimkent; UDC 66.071.7:628.928]

[Abstract] The effect of eddy zones on the intensity of dust separation and combustion were examined. Specifically, he has examined the design and operation of a series of wet-type dust collectors that he helped create in an attempt to systematize ways of using eddy zones to optimize dust collectors designed for use in various manufacturing processes. The technique of adding additional packed bodies (both secured and not secured) into

the contact zone of wet-type dust collectors is shown to be an effective way of creating eddy zones therein. Devices with a regular movable packing in which the packing (spheres, cylinders, plates, disks) are secured on flexible strings are shown to be among the most promising devices for use in setting up eddy zones in wet-type dust collectors and are especially effective in cases where the particles to be trapped are smaller than 1.5  $\mu\text{m}$ . Specific calculations of the results obtained by increasing the height of the contact zone, increasing the number of contact cells, etc., are presented. The specific values presented demonstrate that the location of turbulizers, their geometric shape, and the degree to which they constrict the air flow are all shown to have a significant effect on the efficiency of dust trapping in wet-type dust removers as well as on the strength of the shock wave that develops in pulse chambers (shock wave generators). Figures 6; references 19: 14 Russian, 5 Western.

**Electrochemical Addition of Fluorosulfonic Acid to Perfluor-2-methyl-3-isopropylpentene-2**

927M0167H Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 5, May 92 (manuscript received 8 May 91 after revision 12 Nov 91) pp 1208-1210

[Article by E. A. Avetisyan, A. F. Aerov, V. F. Cherstkov, B. L. Tumanskiy, S. R. Sterlin, and L. S. German, Elementoorganic Compounds Institute, Moscow; UDC 541.12.038:541.138.2:541.515:547.464.161]

[Abstract] Electrolysis of fluorosulfonic acid in the presence of fluoroolefins is one of the most effective methods for introducing the  $\text{FSO}_3$ -group into a fluorocarbon chain. In all known examples, formation of organic reaction products results from either of two anode processes: a) oxidation of the  $\text{FSO}_3$ -anion resulting in formation of peroxydisulfuryldifluoride and subsequent addition of this compound to a fluoroolefin, or b) at lower potential values - oxidation of double bond in the olefin and reaction of the resulting cation-radical with the  $\text{FSO}_3$ -anion. In the present work it was demonstrated that electrolysis of  $\text{HSO}_3\text{F}$  in the presence of perfluoro-2-methyl-3-isopropylpentene-2 leads to formation of  $\text{HSO}_3\text{F}$  addition products at the double bond: 2-hydro-3-fluorosulfateo-perfluoro-2-methyl-3-isopropylpentane and 2-fluorosulfateo-3-hydroperfluoro-2-methyl-3-isopropylpentane. Formation of monofluorosulfates apparently also includes a stage of single electron reduction in the initial olefin. References 6: 2 Russian, 4 Western.

**Electrode Processes in the Electrolysis of Fluorosulfonic Acid. Special Features of the Electrochemical Behavior of Glassy Carbon in Fluorosulfonic Acid**

927M0169A Moscow ELEKTROKHIMIYA in Russian Vol 28 No 6, Jun 92 (manuscript received 25 Mar 91; after revision 21 Nov 91) pp 864-869

[Article by V.A. Grinberg, L.S. Kanevskiy, Ye.G. Cheblakova, V.M. Mazin, A.V. Dribinskiy, V.F. Cherstkov, S.R. Smerlin, and Yu.B. Vasilyev, Electrochemistry Institute imeni A.N. Frumkin, Russian Academy of Sciences, Moscow; UDC 541.135.2]

[Abstract] The methods of cyclic voltammetry and impedance together with x-ray photoelectron spectroscopy and x-ray fluorescence analysis were used to study the special characteristics of the electrochemical behavior of glassy carbon in fluorosulfonic acid. The electrochemical studies were performed as described elsewhere. A 1255 frequency analyzer with a 1275 electrochemical interface (manufactured by Solartron) was used to take the impedance measurements at frequencies ranging from 0.001 to 50 Hz. All potentials were measured and adjusted in relation to a reversible hydrogen electrode in the same solution. After anodic treatment in fluorosulfonic acid, the glassy carbon specimens were extracted from the electrolyte, carefully rinsed in air with bidistillate, dried

in a vacuum extractor at room temperature for 3 hours, and then subjected to spectral studies. Preliminary experiments had shown that the length of time for which specimens were held after anodic treatment before the process of recording the spectra was begun had virtually no effect on the spectral analysis results. An XSAM-800 with  $\text{MgK}_\alpha$  ( $h\nu = 1,254.6$  eV) was used to record the specimens' x-ray photoelectron spectra. The studies performed established that when glassy carbon is subjected to anodic polarization in fluorosulfonic acid, its surface is modified by the fluorosulfate. It is this modification that is evidently responsible for the fact that glassy carbon has a greater electrocatalytic activity than platinum does in the oxidation of  $\text{FSO}_3^-$  in fluorosulfonic acid. At the same time, a passivation of the glassy carbon's surface occurs that gives it a high corrosion resistance in anodic processes in the range of high positive potentials. Figures 7; references 11: 7 Russian, 4 Western.

**The Electrochemical Reduction of 1,1,1-Trichloro-2-Oxy-4-Methylpentene-4 on a Lead Cathode**

927M0169C Moscow ELEKTROKHIMIYA in Russian Vol 28 No 6, Jun 92 (manuscript received 06 May 91; after revision 3 Oct 91) pp 893-899

[Article by L.F. Filimonova, S.M. Makarochkina, I.N. Chernykh, V.G. Soldatov, G.V. Motsak, and A.P. Tomilov, State Russian Scientific Research Institute of Organic Chemistry and Technology, Moscow; UDC 541.438.3:547]

[Abstract] It is known that 1,1-dichloro-4-methylpentadiene-1,4 [diene-1,4] is an intermediate product for the synthesis of the broad-spectrum insecticide permethrin. One way of producing diene-1,4 is electrochemical dehydroxydehalogenation of 1,1,1-trichloro-2-oxy-4-methylpentene-4. The authors of the study reported herein conducted a detailed examination of the process of electrochemical reduction of 1,1,1-trichloro-2-oxy-4-methylpentene-4 in aqueous-organic solvents on a lead cathode. Their primary objective in so doing was to develop a regimen that would be suitable for producing diene-1,4 on a commercial scale. All of the experiments were conducted in a filter-press-type diaphragm electrolyzer. An MK-40L diaphragm was used to separate the anode and cathode spaces. Type S-1 lead was used as a cathode. The cathode surface had an area of  $50 \text{ cm}^2$ , and 200 ml of catholyte was used. The cathode of the consolidated electrolyzer was made of type C-O lead, 15 ml of catholyte was used, and the cathode surface had an area of  $900 \text{ cm}^2$ . An LKhM-80 chromatograph was used to analyze the organic and water-methanol layer, as well as to analyze the methanol and water content. Elemental analysis and IR and PMR spectroscopy were also used to analyze the reaction product. The studies performed established that the reduction of 1,1,1-trichloro-2-oxy-4-methylpentene-4 on a lead cathode leads to the formation of two products—diene-1,4 and 1,1-dichloro-2-oxy-4-methylpentene-4.

The electrolysis conditions used were found to have a significant effect on the ratio in which the two products are formed. An acidic medium and the use of aliphatic alcohols (methyl and isopropyl) were found to facilitate the associated splitting off of chlorine and hydroxyl. The accumulation in the catholyte of diene-1,4 above a certain threshold amount was found to induce a change in the direction of the electrochemical reaction. The

following conditions were found to result in a greater than 70% yield of diene-1,4 (a greater than 70% current efficiency): initial concentration of HCl,  $\leq 3\%$ ; initial concentration of 1,1,1-trichloro-2-oxy-4-methylpentene-4, 15 to 19%; water content, 6 to 25%; methanol, 53 to 73%; current density, 1,000 A/m<sup>2</sup>; and process temperature, 20 to 25°C. Figures 2, tables 8; references 3: 2 Russian, 1 Western.

**The Use of Optically Transparent Cellulose Membranes for the Concentration and Direct Photometric Determination of Metal Traces**

927M065A Kiev *KHIMIYA I TEKHOLOGIYA VODY* in Russian Vol 14 No 6, Jun 92 (manuscript received 10 Jan 92) pp 412-417

[Article by A.T. Pikipenko, A.V. Terletskaia, T.A. Bogoslovskaya, and G.S. Matsibura; UDC 546.426]

[Abstract] A simple and highly sensitive method for the concentration and direct photometric determination of metal traces was developed. The new method is based on the use of optically transparent cellulose membrane ultrafilters (films) that have been modified by organic chromogenic reagents. Vladipor UAM-75 to UAM-200 membrane ultrafilters that had been precut into 6-cm<sup>2</sup> planes and stored in bidistillate were used for the experiments. Solutions of  $2 \times 10^{-3}$  M Michler's thio ketone,  $1 \times 10^{-3}$  M H<sub>2</sub>Dz, and  $2 \times 10^{-3}$  M 2-pyridyl-1-azonaphthol were prepared by dissolving weighed portions of the respective reagents in dimethylformamide [DMFA]. The Dithizone was acidified with sulfuric acid. The starting 1-mg/l metal salt solutions and the working solutions with the required concentration were prepared daily from reagents that were all graded either chemically pure or ultrapure and from bidistilled water. The membranes were modified by placing them in a mixture of water and a solution of the respective reagent in dimethylformamide. Between 20 and 30 ml of mixture was required to tint 30 to 40 membrane strips (180 to 240 cm<sup>2</sup>). The Dithizone-modified films were stored in an aqueous solution with a pH of 2. The tinted films were carefully rinsed with water and stored in bidistillate in darkness. The amount of reagent absorbed by the film was determined photometrically after dissolution of the film in DMFA. A Specol-10 spectrometer was used to measure the optical density of the tinted films against standard untinted film. The studies performed established that the sorption of Michler's thio ketone and 2-pyridyl-1-azonaphthol films does not depend on the pH of the water-DMFA mixture in the respective intervals from 3.5 to 10 and 6.0 to 10.0. The conditions for modifying the cellulose membranes with Dithizone were found to be optimal when the reagent is in molecular form (i.e., with a pH of 2 to 4). It was discovered that Dithizone in ionic form (i.e., Dithizone formed when the pH is above 6) is not retained by the film. The principle of the interaction of the modified films with metal ions in aqueous solutions was found to be as follows. The modified films in aqueous solutions of metal salts measure coloration thanks to the formation of complexes on the surface of the solid phase. In the case of a surplus of metal ions, the film acquires the color of the respective complex. From an absorption spectra standpoint, the resultant complexes are analogous to those obtained in aqueous-organic solutions. The intensity of coloration of

the modified films in the presence of metal salts was found to depend on pH, shaking time, solution temperature, and concentration of metal. The new detection method may be used to detect traces of metals in concentrations as low as 0.5 µg/l in 0.25 l of specimen and has a relative standard deviation of 0.10 to 0.15 ( $n = 5$ ;  $P = 0.95$ ). Figures 4, tables 3; references 14: 9 Russian, 5 Western.

**Product Composition and Reaction Mechanism of Ozone with 2,6-Di(ter-butyl)-4-methylphenol**

927M0167G Moscow *IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA* in Russian No 5, May 92 (manuscript received 5 Jun 91) pp 1203-1207

[Article by S. D. Razumovskiy, M. L. Konstantinova, and G. Ye. Zaikov, Chemical Physics Institute imeni N. N. Semenov, Moscow; UDC 542.943.5:547.5:547.565]

[Abstract] Ozone reacts with phenol to form a variety of products, 60 percent of which result from the rearrangement of the primary complex and introduction of ozone in the aromatic ring in position nearest to the phenol oxy group. In the present work it was demonstrated that ozone also reacts with 2,6-di(ter-butyl)-4-methylphenol to form two series of products resulting both from an opening of the aromatic ring and from its remaining intact. A reaction mechanism is proposed. Figure 1; references 8: 7 Russian, 1 Western.

**Proceedings of Second All-Union Conference 'Ozone - Derivation and Applications'**

927M0175A Moscow *ZHURNAL FIZICHESKOY KHIMII* in Russian Vol 66, No 4, Apr 92 pp 865-866

[Article by V. V. Lunin and N. A. Novikova]

[Abstract] The title conference was held at Moscow State University 30 Apr - 2 Feb 1991. Thirty plenary and section reports and 134 standing reports were presented. The conference reflected the growing interest in further research on the preparation and use of ozone in various fields. Reports were presented in three sections: 1) electrosynthesis, modern designs in ozonators, processes, and equipment; 2) applications of ozone in various branches of the national economy (organic and inorganic syntheses using ozone, ozonolysis, and ozone in medicine); 3) ecological aspects of ozone (water treatment and off-gases). The conference was opened by Orgkom Chairman V. V. Lunin. Plenary reports are published in this current issue (Vol 66, No 4, Apr 92) of *ZHURNAL FIZICHESKOY KHIMII*. At the concluding session of the conference a resolution was adopted on the need for coordination of work on preparation and applications of ozone and the need to convene another All-Union conference in two years.



**Oxidation of Aromatic Compounds with Ozone**

927M0175B Moscow *ZHURNAL FIZICHESKOY KHIMII* in Russian Vol 66, No 4, Apr 92 pp 867-870

[Article by V. A. Ykobi, Chemical Technological Institute, Dnepropetrovsk; UDC 542.943.5]

[Abstract] The need to resolve a number of ecological problems and to develop low-waste technological processes has led to a steady growth in interest in ozone chemistry, especially the search for highly selective ozonizing processes. One of the more promising trends in this area is catalytic oxidation with ozone. Here, the nature of the solvent has a significant influence on kinetics and selectivity. In aqueous solution, the rate of oxidation of a number of aromatic compounds is three times higher than in carbon tetrachloride. Addition of certain organic substances can lower the oxidation rate of aromatic compounds in water by hundreds of times. Hydroxylation takes place during oxidation of benzene, sodium benzene-sulfonate, benzoic acid, and certain other aromatics. The resulting phenols are unstable intermediates in equilibrium concentration. Oxidation of aromatic compounds with ozone in aqueous solution is a complex process involving a series of molecular and radical reactions. A chain mechanism based on experimental data is presented. Use of organic solvents in ozone oxidation attracted interest because in many cases the low solubility of aromatic compounds in aqueous solutions inhibits selective oxidation. However, the selection of suitable solvents is very limited not only as a result of the high reactivity of ozone, but also due to the formation of hydroxyl radicals which react less selectively than ozone, and it is almost impossible to create conditions where the organic solvent is inert to the action of hydroxyl radicals. However, if the hydroxyl radical-solvent reaction does not interfere with the oxidized state of the catalyst, then conditions may be created whereby selective oxidation of aromatic compounds can take place.

**Utilizing Alkene Ozonolysis in Synthesis of Insect Juvenoids and Pheromones**

927M0175C Moscow *ZHURNAL FIZICHESKOY KHIMII* in Russian Vol 66, No 4, Apr 92 pp 886-888

[Article by V. N. Odinkov and G. A. Tolstikov; UDC 547.313+542.949.5]

[Abstract] Research on ozonolysis of alkenes during the past 20 years has opened up the possibility of selectively conducting this reaction as a convenient method for fine organic synthesis. Ozonolysis of cyclic olefins has made it possible to prepare  $\alpha,\omega$ -bifunctional compounds having varying reactivities of their functional groups. Individual isoprenoid blocks of (Z)- or (E)- configuration may be obtained readily by partial ozonolysis of rubbers or gutta-percha. Individual blocks were isolated by fractional distillation which were then used in the synthesis of pheromones and higher membrane-active polyprenols. An entire series of insect pheromones and

juvenoids were synthesized from the bifunctional unsaturated products of ozonolysis of 1,3-dienes. The product resulting from partial ozonolysis of 1,5-dimethylcyclooctadiene was used to synthesize pheromones and juvenoids of isoprenoid or mixed isoprenoid-acetogeninic structure.

**Ozone Methods for Lowering Toxicity of Gases**

927M0175D Moscow *ZHURNAL FIZICHESKOY KHIMII* in Russian Vol 66, No 4, Apr 92 pp 889-893

[Article by G. S. Stolyarov, Kiev Polytechnic Institute; UDC 66.074]

[Abstract] Technological problems associated with decreasing the oxides of nitrogen content and other harmful ingredients in exhaust gases are well known, while traditional absorption methods using air oxygen as an oxidant require large reaction volumes and difficulties with regeneration of spent solutions. The ozone method appears to be the most useful from the standpoint of intensifying the oxidation of nitrogen oxides. In the present work test data and theory are presented together with reaction mechanisms.

**Use of Ozone for Local Treatment of Industrial Effluent**

927M0175E Moscow *ZHURNAL FIZICHESKOY KHIMII* in Russian Vol 66, No 4, Apr 92 pp 894-898

[Article by S. N. Bursova; UDC 628.34]

[Abstract] Serious ecological problems have arisen owing to the prolonged contamination of water reservoirs with untreated or insufficiently treated effluents. For this reason the various sanitation organizations initiated strict regulation of the quality of industrial effluents entering municipal sewage systems in regard to both overall indicators and the content of individual chemical compounds. One way to improve water conservation measures is to set up a common stream of industrial effluents using oxidizing methods for local pretreatment of effluents before entering the municipal system. Various methods of such local pretreatment using ozone are discussed.

**Applying Chemosorption Theory for Analysis and Description of Ozonization Processes of Water and Effluents**

927M0175F Moscow *ZHURNAL FIZICHESKOY KHIMII* in Russian Vol 66, No 4, Apr 92 pp 899-903

[Article by R. R. Munter, S. B. Kamenev, and E. K. Siyrde, Tallin Technical University; UDC 628.543.34]

[Abstract] Separate study of the hydrodynamics and especially the chemical kinetics of a given process together with a knowledge of the laws of mass transfer frequently permits one to proceed to industrial equipment by using mathematical modeling and by-pass the pilot plant stage. In order to implement a differential

approach to ozonizing reactors it becomes necessary to study both chemical kinetics and mass transfer of ozone as well as the combination of the two, i.e. consider the ozonization process as a chemisorption

process consisting of separate stages (modes) in the overall case. In the present work kinetic parameters for certain rapid and slow ozonization reactions are presented. Figure 1; references 3: 1 Russian, 2 Western.

### Determination of the Isotope Composition of Nitrogen in Small (5-10-g) Samples on a MI-1201V Mass Spectrometer

927M0171B Moscow AGROKHIMIYA in Russian No 3, Mar 92 (manuscript received 9 Jul 91) pp 82-84

[Article by N.A. Savidov, Yu.A. Semenov, and B.A. Yagodin, Moscow Agricultural Academy; UDC 543.42.062:543.846]

[Abstract] The use of Rittenberg vessels made of molybdenum glass to determine the isotope composition of nitrogen in small (5 to 10- $\mu$ g) samples is fraught with significant errors. Attempts to boil the vessels in a soda solution were unsuccessful in increasing analysis precision because more of the nitrogen placed into the reaction chamber was absorbed, which in turn made it impossible to obtain an intensity of the lines corresponding to the masses 28 and 29 that was adequate for determination of isotope composition. One technique that has, however, proved successful from the standpoint of reducing the error in determining the isotope composition of nitrogen has been the use of smaller Rittenberg vessels made of quartz. When samples containing less than 100  $\mu$ g nitrogen were used in the smaller-sized quartz vessels, the amount of sodium hypobromide was reduced accordingly from 1.0 to 0.2 cm<sup>3</sup>, and the amount of test sample used was reduced from 2-3 to 0.2 cm<sup>2</sup>. The sodium hypobromide solution was degassed before use to keep it from being thrown over into the reaction vessel along with the sample. Using the new smaller quartz vessels as described made it possible to reduce the relative error in measuring the isotope composition of nitrogen from 7.68 to 0.01%. Tables 2; references 5 (Russian).

### Typical Nitrogen Transformation and Balance in Chernozem Soil When Applied by the Broadcast and Local Methods

927M0176A Moscow AGROKHIMIYA in Russian No 1, Jan 92 (manuscript received 22 Feb 91) pp 12-16

[Article by A.I. Fateyev, Ukraine Soil Science and Agrochemistry Scientific Research Institute imeni A.N. Sokolovskiy, Kharkov; UDC 631.84:631.816.3:631.445.4]

[Abstract] <sup>15</sup>N was used to investigate the dynamics of the transformation and balance of nitrogen in chernozem soils when nitrogen-containing fertilizers are applied by the broadcast and local application methods. The chernozem soil studied is considered typical of the Levoberezhye area of Ukraine. The studies were conducted in 1986, 1987, and 1990 in a series of vegetation tests. The soil samples used were found to have a pH of 6.1 and contain the following: 5.5% humus; 0.33% total nitrogen; 0.16% total phosphorus; and 23 mg/100 g exchange potassium. <sup>15</sup>NH<sub>4</sub>NO<sub>3</sub> ammonium nitrate with an enrichment of 40 atomic percent was used in the 1986 tests, and ammonium nitrate with respective enrichments of 20 and 95.6 atomic percent were used in

the 1987 and 1990 tests. Comparative analyses were performed on the following soil samples: 1) soil with no fertilizer (the control); 2) soil broadcast with <sup>15</sup>NPK; 3) soil to which <sup>15</sup>NPK had been applied locally; and 4) soil that had received a local application of <sup>15</sup>N and been broadcast with PK. In the 1986 tests 286 mg of fertilizer was applied per vegetation vessel, whereas 565 mg fertilizer per vegetation vessel was used in 1987 and again in 1990. During the broadcast trials, the fertilizers were mixed with all of the soil; in the local applications, a strip of fertilizer 2 cm wide was placed at a depth of 6 cm. Mixed samples were taken from the broadcast areas. In the case of the areas that received local application, samples were taken from soil above and below the fertilizer strip. The soil analyses performed established that when nitrogen fertilizer is applied locally, a focus with an elevated concentration of nitrogen in ammonium form remains in the soil for an extended time period. No significant differences in the crop yields of the different soils were observed. Nevertheless, the <sup>15</sup>N utilization was better in the case of local application (51.3% in the case of broadcast application versus 59.4% to 62.5% in the case of local application). Local application of nitrogen fertilizers was thus found to result in better feeding of the soil and in a reduction in the amounts of nitrogen lost from soil. The studies further revealed that higher <sup>15</sup>N utilization factors result when nitrogen fertilizers are applied locally together with phosphorus and potassium fertilizers than when nitrogen fertilizers are applied alone. The fraction of "extra" nitrogen used after local application was also less than the fraction used after broadcast application (25.5% in the case of broadcast application versus 24.0 and 19.6% after local application). Other studies have demonstrated that use of the local application technique actually causes an increase in the percentage of "extra" nitrogen used in soddy podzolic soil. In view of this fact, the researchers concluded that utilization of "extra" nitrogen depends on both soil type and nitrogen availability. The longer existence of foci of elevated concentrations of nitrogen in ammonium form in soils to which the fertilizer had been applied locally was attributed to inhibition of nitrification when the local application technique is used. Tables 6; references 8 (Russian).

### Crop Yield and Quality in Crop Rotation With a Balanced Fertilization System as a Function of the Phosphorus and Potassium Content in the Soddy Podzolic Sandy Loam Soil of Western Byelarus. Part 3. The Quality of Products of Crop Rotation

927M0176B Moscow AGROKHIMIYA in Russian No 1, Jan 92 (manuscript received 3 May 89) pp 17-29

[Article by V.D. Sudakov, A.I. Dylko, Z.A. Polyukh, L.L. Kuzar, G.K. Dubeyko, G.A. Verbitskaya, and V.G. Shereshevets, Brest Oblast Planning and Surveying Station for the Chemicalization of Agriculture; UDC 631.811.2:631.811.3:631.445.24.631.582(476.7)]

[Abstract] A multiyear (1972 through 1987) investigation was conducted of the crop yield and quality

resulting from a regimen of crop rotation with a balanced fertilization system as a function of phosphorus and potassium concentration in the soddy podzolic sandy loam characteristic of western Byelorussia. In this third part of their series of publications on the multiyear trials, the authors concentrate their attention on the quality of products resulting from the use of crop rotation. The studies performed established that in soddy podzolic sandy loam, the maximum yield of feed units and protein was obtained in fertilization regimens including the addition of 10 to 15 mg  $P_2O_5$  and  $K_2O$  per 100 g soil (530  $\pm$  100 kg/hectare) and N60P4K115 in a background of 10 t/hectare peat-manure compost on average per rotation. The yields from such a regimen amounted to 70 centners and about 800 kg/hectare per year, respectively. Each feed unit thus obtained contained an average of 85 to 86 g digestible protein, which represents a 7 to 9% higher productivity than achieved from other fertilization regimens. Crop rotation also resulted in a high feed productivity in other fertilizer regimens with equally high concentrations of  $P_2O_5$  and  $K_2O$  when the two fertilizers were used in a 1:1 ratio or thereabout. The change in crops' feed productivity and hence in crop rotation productivity was found to depend not as much on plants' chemical composition as on plant yields. An analysis of the relative importance of the amount of nitrogen fertilizer used, weather, and soil reserves of PK to total feed units produced established that the fraction of nitrogen fertilizer used was 44% responsible, weather was 42% responsible, and soil reserves of PK were 6% responsible. The changes in the quality of products produced by using crop rotation that were discovered during the course of the multiyear study were attributed primarily to the products' protein content, which was in turn dictated primarily by the use of nitrogen fertilizers. Nitrogen fertilizers were found to increase a plant's protein content by 11 to 14%. The effect of the amount of PK stored in soil turned out to be insignificant. The content of feed units and exchange energy (in MJ) per kilogram of dry mass was found to be the same in each crop studied and to fluctuate within the bound of  $\pm$  1% depending on the effect of soil nutrients and fertilizers. Tables 9; references 29 (Russian).

**The Barley Yield in Leached Chernozem Soils and the Removal of Basic Nutrients as a Function of Doses of Mineral and Lime Fertilizers**

927M0176C Moscow AGROKHIMIYA in Russian No 1, Jan 92 (manuscript received 28 Jun 91) pp 50-59

[Article by N.P. Bogomazov, N.M. Soldatov, S.M. Soldatov, and Ye.I. Blagina, Central Chernozem Affiliate, All-Union Fertilizers and Agropedological Scientific Research Institute imeni D.N. Pryanishnikov, Belgorod; UDC 631.82:631.821.1:633.16:631.445.4]

[Abstract] A three-factor field test was conducted to determine the direct effect of increasing nitrogen doses and the aftereffect of phosphorus, potassium, and lime on the yield and quality of barley grown in a sugar

beet-barley crop rotation regimen in the leached chernozem soils characteristic of Russian's central chernozem area. The removal of nutrients per unit product as a function of the doses of the aforesaid fertilizers was also studied. The plowed layer of soil studied was characterized by the following agrochemical indicators: humus, 5.1 to 5.2%; alkali-hydrolyzed nitrogen, 117 to 150 mg/kg; mobile phosphorus, 86 to 100 mg/kg; exchange potassium, 104 to 133 mg/kg; pH, 4.9 to 5.3; total absorbed bases, 29.8 to 35.4 mg-Eq/100 g soil; hydrolytic acidity, 4.6 to 5.2 mg-Eq/100 g soil, and exchange calcium, 26.2 to 30.6 mg-Eq/100 soil. Defecated sugar juice from the Chernyanka Sugar Plant was used as the lime fertilizer. It had a moisture content of 17.6 to 17.9% and contained 36.3 to 42.6%  $CaCO_3$ . Ammonium nitrate, double superphosphate, and potassium salt were used as mineral fertilizers. The unit dose under each sugar beet amounted to N90P90K90. Only nitrogen fertilizers were applied under the barley (in a unit dose of N30). The barley also utilized the aftereffect of the phosphorus, potassium, and lime fertilizers applied when the sugar beets were grown. The test fertilizer regimen consisted of 64 different variations of the fertilization routine in all. On the basis of the studies performed, the researchers concluded that the optimal dose of nitrogen for brewing barley is 75 to 85 kg/hectare, whereas the optimal dose for feed barley is 90 kg/hectare. The aftereffects of phosphorus-potassium and lime fertilizers appeared to result in an increase in yield but to have little impact on grain yield or quality. The concentration of nutrients in the grain and straw were found to depend on meteorological conditions. Under drought conditions, the grain's and straw's nitrogen content increased while its phosphorus and potassium contents decreased. The use of mineral fertilizers turned out to have a significant effect on removal of basic nutrients per unit basic product and on the respective amount of resultant by-product. The addition of nitrogen fertilizers to the soil increased the amount of nutrients in both the grain and straw. Phosphorous, potassium, and lime fertilizers had a lesser effect on the entry of nitrogen, phosphorus, and potassium into the barley and its by-products. When nitrogen was added to the soil, the amount of nutrients removed to the barley increased by 3 to 9 kg, and the removal of potassium increased by 1.1 to 3.5 kg per 10 centners of product. Nitrogen fertilizers were also found to help reduce phosphorus removal per unit yield by 0.19 to 0.57 kg. Tables 8; references 28 (Russian).

**The Effect of Heavy Metals on the Electrokinetic Potential of the Silt Fraction of Gray Forest Soil**

927M0176D Moscow AGROKHIMIYA in Russian No 1, Jan 92 (manuscript received 5 Jul 91) pp 80-83

[Article by O.A. Trubetskoy, B.N. Zolotareva, V. Strnad, M. Khaynos, and L. Kholish, Soil Science and Photosynthesis Institute, USSR Academy of Sciences, Pushchino, Moscow Oblast, and Agrophysics Institute, Poland



Academy of Sciences; UDC 631.416.8:631.425.7:631.445.25]

[Abstract] Heavy metals from technogenic atmospheric emissions have been demonstrated to accumulate in the upper layers of soil in the following amounts (g/ha/y): Cd, 19; Cu, 136; Pb, 4,709; and Zn, 1,098. Those surface properties of soils that are tied to the charge of the individual soil particles represent the most important factor dictating the soil's capacity to adsorb heavy metal cations. In view of these facts, the authors of the study reported herein examined the effect of heavy metals on the electrokinetic potential ( $\zeta$ ) of the silt fraction of gray forest soil. The gray forest soil studied was taken from under natural plant life (pH, 5.7  $\pm$  0.1), had a  $\zeta$ -potential of 18 mV, and contained the following amounts of heavy metals (mg/kg soil): Cu, 5.0; Pb, 10.0; Zn, 60.0; and Cd, 0.3. The model experiment conducted was set up in the forest in bottomless vessels. The vessels were presterilized polyethylene packs with a capacity of 5 kg each. At the site where the experiment was to be conducted, a narrow trench was dug to the depth of the humus-accumulative layer. The mass removed was homogenized and weighed into 5-kg portions. Metal salts were added to the soil mass for each vessel individually, and after careful mixing, each of the separate batches of soil was poured into a vessel. The vessels were then placed in the trench, slit, and covered with the remaining soil to the level of the surface. The doses in which the nitric acid metal salts had been added to the individual vessels were as follows (mg metal/kg soil): Cu and Pb, 1 to 100; Zn, 1 to 300; and Cd, 1 to 25. The vessels were left in place for 2 years, after which samples were taken from each of them. Studies performed on the soil samples established that the presence of heavy metals in the silt fraction of gray forest soil helps lower the value of the soil's  $\zeta$ -potential as compared with that of control soils. In the samples of silt fraction containing Pb and Cd, the  $\zeta$ -potential was significantly lower than that of the samples containing Zn and Cu. In all cases, increases in the amount of heavy metals in the soil samples were found to be accompanied by a reduction of the given sample's  $\zeta$ -potential. The effect of the heavy metals was attributed to the fact that they react primarily with the organic matter rather than the mineral component of the soil. Table 1; references 10: 7 Russian, 3 Western.

**The Distribution of  $^{238}\text{U}$  and  $^{232}\text{Th}$  in Soils and Plants and the Effect of Fertilizers on the Accumulation of These Radionuclides in Agricultural Harvests Under the Conditions of Azerbaijan**

927M0176E Moscow AGROKHIMIYA in Russian No 1, Jan 92 (manuscript received) pp 84-90

[Article by D.A. Aliyev, T.D. Gyulaliyev, and R.M. Aleksakhin, Azerbaijani Agriculture Scientific Research Institute, Baku, and All-Union Agricultural Radiology Scientific Research Institute, Obninsk; UDC 632.118.3:546.791:546.841:631.41:631.8]

[Abstract] The distribution of  $^{238}\text{U}$  and  $^{232}\text{Th}$  in the main types of soils of Azerbaijan and in plants grown in those soils was examined. They further examined the effect that fertilizers have on the accumulation of  $^{238}\text{U}$  and  $^{232}\text{Th}$  in agricultural crops under the conditions of Azerbaijan. Samples of six different types of soils were analyzed: cinnamon leached, chestnut (gray-cinnamon), chestnut, gray-brown, light chestnut, and dark chestnut. The concentration of  $^{238}\text{U}$  was found to range from 12.6 to 48.6 Bq/kg in these different types of soil, while the concentration of  $^{232}\text{Th}$  was found to range from 11.4 to 39.0 Bq/kg. The highest concentrations of  $^{238}\text{U}$  were found in the cinnamon leached and light chestnut soils (48.6 Bq/kg) and the lowest were in gray-brown soil (12.6 Bq/kg). The highest concentrations of  $^{232}\text{Th}$  were found in cinnamon leached soils (39.6 Bq/kg) and light chestnut soil (39.0 Bq/kg), and the lowest concentration were found in the chestnut (gray-cinnamon) soil. The concentrations of mobile forms of  $^{238}\text{U}$  (water-soluble, exchange, and oxygen-soluble) in the study soils were higher than those of  $^{232}\text{Th}$ . The maximum concentrations of water-soluble and exchange forms of  $^{238}\text{U}$  were found in chestnut (gray-cinnamon), chestnut, and gray-brown soils. A close inverse dependence between the concentration of water-soluble and exchange forms of  $^{238}\text{U}$  and the content of humus and exchange potassium in the soil samples was discovered. Water-soluble forms of  $^{232}\text{Th}$  were absent from the cinnamon, leached, light chestnut, and chestnut (gray-cinnamon) soils. The highest concentrations of exchange forms of  $^{232}\text{Th}$  were found in the gray-brown and chestnut soils. Plants were found to accumulate  $^{238}\text{U}$  much more intensively than  $^{232}\text{Th}$ . The coefficients of the accumulation of  $^{238}\text{U}$  were found to range from 0.8 to  $4.4 \times 10^{-3}$  in wheat and barley grains and from  $2.8$  to  $7.6 \times 10^{-3}$  in straw. The concentration of  $^{238}\text{U}$  in wheat and barley grown in chestnut (gray-cinnamon) soil was a factor of 2.2 to 2.6 higher than that in plants grown in gray-brown soil. The concentration of  $^{232}\text{Th}$  in barley and wheat crops grown in gray-brown soil was a factor of 2.1 to 3.0 higher than in the same crops grown in cinnamon leached soil. The concentrations of  $^{238}\text{U}$  and  $^{232}\text{Th}$  in the vegetative and generative portions of wheat and barley were found to be closely linked to the content of exchange calcium, mobile phosphorus, and the forms in which radionuclides were present in the soil. The application of mineral fertilizers (in both customary and elevated amounts) was found to have a relatively small effect on the concentration of  $^{238}\text{U}$  in the grain and straw of grassy and leguminous plants. In the case of  $^{232}\text{Th}$ , however, increases in the amount of mineral fertilizer used were associated with somewhat of a decrease in radionuclide concentrations in plants and a slight increase in removal from the crop. As the fertilizer dose was increased, the concentration of  $^{238}\text{Th}$  [sic] in soy, chick pea, barley, and wheat yields decreased by a factor of 1.1 to 1.4, and the concentration of  $^{232}\text{Th}$  decreased by a factor of 1.1 to 2.0. Figure 1, tables 4; references 8 (Russian).



**Effect of Non-traditional Meliorants on Crop Harvest, Quality of Agricultural Produce, Soil Properties, Consumption and Transfer of Nutritives. Report 1. Comparative Evaluation of Non-traditional Chemical Methods**

927M0192A Moscow AGROKHIMIYA in Russian No 2, Feb 92 (manuscript received 5 Jan 91) pp 87-96

[Article by V. F. Arshavskaya and T. I. Savchenko, Design and Technological-Planning Soil Melioration SRI (AU); UDC 631.821]

[Abstract] Liming acid soils plays a leading role in the agricultural technology of high and stable crop yields. Excessive soil acidity not only presents unfavorable conditions for plants, but also lowers the efficiency of mineral fertilizers. Liming also has an environmental impact in compensating for losses in calcium and magnesium, depleted by harvesting and atmospheric precipitation. In many regions of the country the tempo of

liming is held back due to shortages in lime. These shortages could be minimized by substituting carbonate-containing industrial wastes such as from the Transbaltic State Electric Power Plant and the Achinsk Clay Combine, which now has reserves exceeding 30 million tons of belite (component of portland cement) sludge. Comprehensive agri-technical and toxicological evaluations of ash-containing waste products have not yet been evaluated, although studies of the effectiveness of milled belite sludge as a chemical meliorant indicate that it is just as effective as lime. However, the toxicological properties of belite sludge have not yet been well studied. In the present work results are presented on the properties of ash and belite sludges in comparison with standard liming. The studies provide a base for deciding on the utilization of secondary resources and the possibilities of effective and ecologically safe application of meliorants made from the above waste products to neutralize acid soils in the non-black soil zone of the RSFSR. References 20 (Russian).

**Sandwich Mono- and Polynuclear Complexes of Transition Metals as Basis for Developing Concept of Inorganic Benzoid Systems**

927M0167D Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 5, May 92 (manuscript received 26 Dec 91) pp 1083-1106

[Article by M. I. Rybinskaya, Elementoorganic Compounds Institute, Moscow; UDC 547.1'13]

[Abstract] Cationic  $\Pi$ -complexes of transition metals are significant as reagents and catalysts in organic and metallorganic syntheses. In recent years sandwich compounds having unique structures such as metallocenonium, multi-decked complexes, and sandwich clusters acquired special interest. Development of synthesis methods and study of properties of these compounds

proved to be fruitful not only because it lead to the preparation of a number of previously unknown cationic complexes of transition metals, but also because it made possible the resolution of several theoretical problems, including that of a concept of metallocenonium ions and new triple-membered metallocyclic benzoid systems. Development of these concepts helped close the gaps between some segments of organic, metalloorganic, and inorganic chemistry. The present article is a review (awarded the 1991 A. N. Nesmeyanov Gold Medal) on the preparation of cationic sandwich compounds of transition metals having unique structures and including metallocenonium, multi-decked complexes, and sandwich clusters. The review covers simple and convenient synthesis methods for cationic  $\Pi$ -complexes of transition metals by ligand exchange in strong protonic acids and other methods. References 79: 26 Russian, 53 Western.

**A Model of the Dynamics of a Filtration Process With Consideration for the Redistribution of Pressures Between the Compressible Cake and Filtration Partition**

927M0168C Moscow *TEORETICHESKIYE OSNOVY KHIMICHESKOY TEKHNologii* in Russian Vol 26 No 3, May-Jun 92 (manuscript received 25 Sep 89) pp 397-405

[Article by Ye.I. Vorobyev, Sugar Industry Scientific Research Institute, Kiev; UDC 66.067]

[Abstract] The existing methods of predicting the properties of cakes produced on filters have all been developed under the assumption that the pressure at the cake-filtration partition interface is constant. This assumption is far from an accurate description of what actually happens in the initial period of a filtration process or when filters are operating in short cycles. In view of the shortcomings of existing filtration process models, the author of the study reported herein developed a mathematical model of the dynamics of the process of filtration with simultaneous consideration for the compressibility of the cake and the redistribution of pressures between the cake and the filtration partition. Consideration of the effect of the filtration partition on filtration is also shown to be important inasmuch as moister cakes are formed when filtration partitions have a high drag (because of the delay in the growth of pressure on the cake particles formed on a filtration partition with a high drag). Analytical solutions are derived that may be used to find the distribution profiles of filtration parameters along the thickness of the cake formed. The formulas have been refined for use in designing an actual filtration process. Figures 5; references 12: 7 Russian, 5 Western.

**The Complexing of Gallium Fluoride With Semicarbazide and Carbonyl Hydrazide in Aqueous Solutions**

927M0172A Moscow *KOORDINATSIONNAYA KHIMIYA* in Russian Vol 18 No 3, Mar 92 (manuscript received 15 Nov 91) pp 243-246

[Article by A.N. Popov, M.G. Ivanov, and I.I. Kalinichenko; UDC 541.49:546.681.268.5]

[Abstract] The method of  $^{19}\text{F}$  NMR was used to study the complexing of gallium fluoride with the hydrazides semicarbazide and carbohydrazide [L] in the systems  $\text{Ga}(\text{NO}_3)_3 \cdot \text{NH}_4\text{F} \cdot \text{L} \cdot \text{H}_2\text{O}$  and  $\text{GaF}_3 \cdot \text{L} \cdot \text{H}_2\text{O}$ . A Varian XL-100 radiospectrometer (94.1 MHz and internal deuterium stabilization) was used to record the  $^{19}\text{F}$  NMR spectra of the study compounds. The chemical shifts occurring in the temperature range from 273 to 255 K were recorded relative to an  $\text{SiF}_6^{2-}$  internal standard and recalculated in relation to  $\text{CFCl}_3$ . All of the solutions used in the studies were based on  $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$  or

$\text{Ga}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$  in accordance with a procedure published elsewhere. The NMR studies performed demonstrated that the reaction of gallium fluoride with acetylhydrazine, semicarbazide, or carbohydrazide results in the formation of the mixed-ligand gallium complexes  $[\text{GaF}_4\text{L}]^-$  and  $\text{GaF}_n\text{L} \cdot \text{aq}^{(3-n)}$  ( $n = 1, 2$ ) with coordination of the hydrazide through the amine atom of the nitrogen and the oxygen of the carbonyl group along with the formation of a five-membered metal cycle. The ion and isomer equilibrium of the composition of the resultant compounds was found to be dictated primarily by the nature of the substituent at the hydrazide grouping and the ratio of ligands to complex-forming agent. The ion  $[\text{GaF}_4\text{L}]^-$  with a nonequivalent arrangement of the acidoligands in the coordination sphere was found to predominate at an F:Ga ratio of 3 and an L:Ga ratio of 2 or greater. Figures 2; references 11 (Russian).

**The Crystalline Structure of Dinitratodiaquo-bis-(Pyracetam)Copper (II)**

927M0172B Moscow *KOORDINATSIONNAYA KHIMIYA* in Russian Vol 18 No 3, Mar 92 (manuscript received 22 Nov 91) pp 292-296

[Article by V.Kh. Sabirov, M.A. Poray-Koshits, Yu.T. Struchkov, A.N. Yunuskhodzhaev, and A.F. Dumatov; UDC 548.737+546.562+547.743]

[Abstract] An x-ray crystallographic study of the complex  $[\text{Cu}(\text{PM})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]$  (where PM = pyracetam, i.e., 2-oxo-1-pyrrolidinylacetamide) was conducted. Specimen crystals were produced from a saturated water-and-acetone solution of the complex. The crystals, which were monoclinic, were found to be characterized by the following indicators at  $-120^\circ$ :  $a = 9.231(2)$ ,  $b = 6.045(1)$ , and  $c = 17.759(4)$  angstroms;  $\beta = 94.70(2)^\circ$ ;  $V = 987.60(6)$  cubic angstroms;  $d = 1.71 \text{ g/cm}^3$ ;  $\mu(\text{MoK}\alpha) = 22.34 \text{ cm}^{-1}$ ;  $Z = 2$ ; and limiting boundary,  $P_2/n$ . The cell parameters and intensity of 2,200 reflections with  $1/\sigma(1)$  were measured on a Siemens RZ/PC automatic diffractometer. The structure was deciphered by the direct method and refined in an anisotropic approximation to the convergence factors  $R = 0.029$  and  $R_w = 0.030$ . The studies performed established that the Cu atom is in the crystallographic symmetry center and has a tetragonal-bipyramidal coordination on account of the O atoms of the acetamide groups of the two pyracetam ligands, two water molecules, and two  $\text{NO}_3^-$  ligands. The Cu-O bond lengths were found to equal 1.963, 1.941, and 2.421(1) angstroms, respectively. The pyrrolidine cycle of the pyracetam was found to have the conformation of a simplified convert. The plane acetamide group was found to be perpendicular to the midplane of the heterocycle, and the coordinated oxygen atom was located in a transoid position relative to the heterocycle's nitrogen atom. The crystal contains four types of hydrogen bonds: one intermolecular H-bond, i.e.,  $\text{N}(2)\text{-H}(1\text{N})\cdots\text{O}(2\text{N})$ , and three molecular H bonds that result in the formation of a three-dimensional skeleton of H-bond molecules in the crystal. Figures 2, tables 4; references 4: 1 Russian, 3 Western.

### The Crystalline and Molecular Structure of bis-(2-Chloro-4-Acetylhexene-1-one-5)-Copper (II)

927M0172C Moscow KOORDINATSIONNAYA KHIMIYA in Russian Vol 18 No 3, Mar 92 (manuscript received 25 Apr 91) pp 303-306

[Article by F.M. Chyragov, I.Ya. Gasanov, D.G. Gambarov, T.Z. Kuliyeva, and M.I. Chyragov, Baku State University; UDC 548.736.5]

[Abstract] A new organic reagent based on acetylacetone: 2-X-4-acetylhexene-1-one-5 (X = Cl, Br) was synthesized. The authors then proceeded to decipher the crystalline structure of bis-(2-chloro-4-acetylhexene-1-one-5)-copper (II). The compound  $\text{Cu}(\text{C}_8\text{H}_{10}\text{O}_2\text{Cl})_2$  was produced by reacting a 0.1 N solution of  $\text{CuCl}_2$  with a 2% solution of 2-chloro-4-acetylhexene-1-one-5 in a 1:2 ratio at a pH of 5. The resultant substance was extracted by  $\text{CCl}_4$ . After 20 days, dark green lamellar monocrystals appeared. A Sintex P2<sub>1</sub> automatic diffractometer was used to determine the parameters of the triclinic cell. The parameters were as follows:  $a = 10.557(3)$ ,  $b = 7.884(2)$ , and  $c = 13.889(5)$  angstroms;  $\alpha = 112.48(2)$ ,  $\beta = 109.52(2)$ , and  $\gamma = 102.57(2)^\circ$ ;  $V = 924$  cubic angstroms; and limiting boundary, P1. The crystal's structure was found to consist of densely packed complex groups bound by an inversion center between which intermolecular interactions are taking place. The crystal was found to be characterized by a comparatively short distance between the two molecules bound at the inversion center ( $\text{Cu}-\text{C}(2.3) = 3.25$  angstroms). This in turn was interpreted as an indication of the formation of weak Cu-C bonds that in turn results in the transition of the plane-square coordination of the copper atom to a tetragonal-bipyramidal coordination. Figure 1, tables 2; references 5: 3 Russian, 2 Western.

### The Crystalline Structure of $\text{NaKSnF}_6$

927M0173A Moscow KOORDINATSIONNAYA KHIMIYA in Russian Vol 18 No 2, Feb 92 (manuscript received 10 Jun 91) pp 129-132

[Article by A.V. Gerasimenko, S.B. Ivanov, T.F. Antokhina, and V.I. Sergiyenko, Chemistry Institute, Far Eastern Department, Russian Academy of Sciences; UDC 546.811.161:548.736]

[Abstract] An x-ray crystallographic examination of  $\text{NaKSnF}_6$  crystals was conducted. The crystals, whose synthesis was described in a previous communication, were studied on the basis of 1,873 reflections obtained by using a diffractometer with  $\text{MoK}_\alpha$  radiation. The  $\text{NaKSnF}_6$  crystals were found to be rhombic and were characterized by the following parameters:  $a = 11.800(2)$ ,  $b = 5.000(1)$ , and  $c = 8.125(1)$  angstroms;  $Z = 4$ ;  $\rho$  (exp) = 3.42 and  $\rho$  (calc) = 3.41  $\text{g}/\text{cm}^3$ ; and limiting boundary,  $\text{Pna}2_1$ . The Sn and Na coordination polyhedra were found to be distorted octahedra with fluorine atoms at the vertices. The Na-F bond lengths ranged from 2.201(3) to 2.518(3) angstroms ( $r(\text{Na}-\text{F}) = 2.308$  angstroms). The studies also established that the Sn and Na

octahedra, which were joined to one another at the ribs and vertices, form a three-dimensional skeleton with  $\text{K}^+$  cations located in its free spaces. All of the cations in the structure were found to be in layers orthogonal to the crystal's z-axis. On the basis of the studies performed, the study  $\text{NaKSnF}_6$  crystals were classified as having an eschynite structure. They can also be looked upon as being perovskite derivatives on account of their crystallographic shift, which results in a shift of both the chain and interchain channel cavities. Figures 2, tables 2; references 9: 7 Russian, 2 Western.

### The Crystalline Structure of (Pyridino)-Hydroethylenediaminetetraacetatocobalt (III) Dihydrate

927M0173B Moscow KOORDINATSIONNAYA KHIMIYA in Russian Vol 18 No 2, Feb 92 (manuscript received 27 Aug 91) pp 133-138

[Article by I.M. Bezrukavnikova, T.N. Polynova, M.A. Poray-Koshits, and A.L. Poznyak, Moscow State University imeni M.V. Lomonosov; UDC 548.736]

[Abstract] An x-ray crystallographic examination of  $[\text{CoHedtaPy}]2\text{H}_2\text{O}$  (where Py = pyridine) was conducted. The complex  $[\text{CoEdtaPy}]^-$  was obtained by reacting  $[\text{CoEdtaPy}]^{2-}$  with pyridine in a mixture of water and dimethylsulfoxide in the presence of activated charcoal. It was sorbed from the reaction mixture on Dowex 1 x 8 anionite and eluted with 0.05 M HCl in a protonated noncharged form of  $\text{CoHedtaPy}$ . Monocrystals were then grown by isothermal evaporation of the eluate. A CAD-4 automatic diffractometer ( $\text{MoK}_\alpha$  radiation) and a graphite monochromator were used for the x-ray crystallographic studies. The  $[\text{CoHedtaPy}]2\text{H}_2\text{O}$  crystals were found to be monoclinic and to be characterized by the following parameters:  $a = 24.229(2)$ ,  $b = 10.568(2)$ , and  $c = 7.122(4)$  angstroms;  $\gamma = 99.51^\circ$ ,  $Z = 4$ , and limiting boundary,  $\text{P}2_1/\text{a}$ . The data were based on 2,369 reflections by using the SHELX program on a YeS-1060 computer. The structure was refined to  $R = 0.04$  in an anisotropic-isotropic approximation. The crystals were found to contain mononuclear molecular complexes with the composition  $[\text{CoHedtaPy}]$  and molecules of crystalline water that were bound to one another by hydrogen bonds. The Co (III) coordination polyhedron was established to be a distorted octahedron formed by oxygen atoms, two nitrogen atoms, an Edta ligand, and the nitrogen atom of the competing Py ligand. The plane of the Co (III) polyhedron that was tentatively selected as the equatorial plane was formed from three nitrogen atoms and an oxygen atom. Two oxygen atoms of the acetal groups of the Edta ligand occupy the axial positions. The protonated acetate branch is not involved in the coordination. The coordination of  $\text{Edta}^{4-}$  and pyridine in the complex  $[\text{CoHedtaPy}]2\text{H}_2\text{O}$  thus corresponds to a *cis*-equatorial isomer as do other complexes of the said type (e.g.,  $[\text{CoEdtaX}]^n$  where  $X = \text{NH}_3, \text{N}_3^-$ ). The presence of a pyridine ring was not found to have any significant

effects on the angle characteristics of the Co (III) polyhedron. Figures 2, tables 4; references 8: 5 Russian, 3 Western.

**The Crystalline Structure of the Dihydrate of Ethylenediaminodisuccinatonicelate (II) of Pentaquozeine**

927M0173C Moscow KOORDINATSIONNAYA KHIMIYA in Russian Vol 18 No 2, Feb 92 (manuscript received 17 Oct 91) pp 150-155

[Article by I.M. Bezrukavnikova, T.N. Polynova, I.B. Kovaleva, A.N. Mitrofanova, and M.A. Poray-Koshits, Moscow State University imeni M.V. Lomonosov; UDC 548.736]

[Abstract] An x-ray crystallographic examination of a complex with the composition  $\text{ZnNiEdds} \cdot 8\text{H}_2\text{O}$  was conducted.  $\text{ZnNiEdds} \cdot 8\text{H}_2\text{O}$  is the fourth complex of nickel (II) with an Edds<sup>4-</sup> ligand that the authors have studied by x-ray crystallographic analysis. The  $\text{ZnNiEdds} \cdot 8\text{H}_2\text{O}$  was synthesized by reacting stoichiometric quantities of the ligand and metal carbonates that had been freshly precipitated from solutions of their salts. The crystals that were subsequently precipitated from aqueous solutions were analyzed on a CAD-4 diffractometer (with  $\text{MoK}_\alpha$  radiation and a graphite monochromator and  $\omega$ -scanning); 4,744 reflections were recorded. The study crystal's structure was deciphered by the heavy-atom method by using the SHELX software package on a YeS-1060 computer and was refined to  $R = 0.08$ . The parameters of  $\text{ZnNiEdds} \cdot 8\text{H}_2\text{O}$  crystals were determined to be as follows:  $a = 30.546(8)$ ,  $b = 15.876(4)$ , and  $c = 9.907(4)$  angstroms;  $\gamma = 110.70(4)^\circ$ ;  $Z = 8$ ; and limiting boundary,  $B2/b$ . The  $\text{ZnNiEdds} \cdot 8\text{H}_2\text{O}$  crystals were found to consist of  $[\text{NiEdds}]^{2-}$  anionic complexes,  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  cationic autocomplexes, and molecules of the crystallization water joined by hydrogen bonds. The nickel coordination polyhedron was found to be a distorted octahedron and to be classified overall as a *trans*-O(5)-isomer. The average lengths of the Ni-O<sub>R</sub>, Ni-O<sub>Q</sub>, and Ni-N bonds were 2.061(8), 2.043(8), and 2.058(8) angstroms, respectively. The average values of the internal angles of the NNiO and NNiN were found to equal 85.5(3) and 86.3(3) $^\circ$  and to thus coincide with the values of analogous angles found in other Edds<sup>4-</sup> complexes within the bounds of the measurement error. The stress level of the metal cycles in complexes of transition metals with an Edds<sup>4-</sup> ligand was measured in terms of the deviation of the sum of the intrachelate angles of the cycle from the analogous values corresponding to an unstressed cycle. An analysis of the measurements obtained indicated that the sum of the intracycle angles in five-membered R-cycles is in all cases less than the sum of the angles corresponding to an ideal cycle, whereas the sum of the angles found in the six-membered R-cycles was in all cases found to be greater than the sum for an ideal cycle. In other words, the stress level of the five-membered cycle is expressed in its extreme corrugation, whereas that of a six-membered cycle is expressed in its reduced corrugation. These conditions were

acknowledged to be very tentative inasmuch as the valence angles at oxygen atoms may vary greatly without any weakening of the bond with the metal. Figure 1, tables 5; references 7: 2 Russian, 5 Western.

**Thermodynamics of Ion Exchange in Zinc Selenide Crystals**

927M0174A Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 66 No 3, Mar 92 (manuscript received 28 Nov 90) pp 605-614

[Article by V.A. Ganshin, Yu.N. Korkishko, and V.A. Fedorov, Moscow Electronics Engineering Institute; UDC 541.121+539.3+621.315.595.4]

[Abstract] The thermodynamics of  $\text{Cd}^{2+}$ - $\text{Zn}^{2+}$  ion exchange in zinc selenide crystals was examined. Wafers of zinc selenide monocrystals with a sphalerite structure and (111) orientation that were grown from a gaseous phase were used in the studies. The wafers were subjected to successive mechanical, chemomechanical, and chemical polishing with a  $\text{CrO}_3\text{HCl}$  etching agent. A mixture of potassium, sodium, zinc, and cadmium sulfates was used as the alloying melt. Only the zinc and cadmium sulfates were active ingredients; the potassium and sodium sulfates served only to reduce the temperature of transition to a liquid state. The  $\text{ZnSO}_4$  (40.7 mol%)- $\text{K}_2\text{SO}_4$  (30.2 mol%) mixture was eutectic ( $t_e = 384^\circ\text{C}$ ), and the small amount of  $\text{CdSO}_4$  additive used did not significantly change the melting point. The alloying melt was a transparent liquid that remained stable in air. The ion exchange structures were formed by lowering the ZnSe wafers into the melt, which was kept at a stabilized temperature of 400 to  $500^\circ\text{C}$ . The interplane distances were determined by x-ray diffraction with a Rigaku Denki D-2 diffractometer, and Auger electron spectroscopy with signal multiplication (with an LAS 2000 Riber spectroscopy) was used to determine the elements throughout the depth of the ion exchange region. These studies, along with determinations of the solid-phase composition and crystalline lattice parameter of the sphalerite CdSe, established that the composition of the surface  $\text{Cd}_u\text{Zn}_{1-u}\text{Se}$  solid solutions did not depend on the time of processing in the melt but was instead unequivocally determined by the ratio of the concentrations of zinc and cadmium sulfates and the process temperature. X-ray phase analysis confirmed that the  $\text{Cd}_u\text{Zn}_{1-u}\text{Se}$  solution formed has a sphalerite structure throughout the entire concentration range studied ( $0 \leq u \leq 1$ ). Because the crystalline lattice parameters of the ion exchange structures of the  $\text{Cd}_u\text{Zn}_{1-u}\text{Se}$  solid solution and the ZnSe substrate differ significantly from one another, the process of obtaining ion exchange structures was accompanied by the development of elastic stresses and relaxations with the formation of a system of misfit dislocations. The thermodynamic ion exchange characteristics of both nonstressed and stressed  $\text{Cd}_u\text{Zn}_{1-u}\text{Se}$  solid solutions, i.e., their equilibrium constants and interchange energies, were determined. The unstressed  $\text{Cd}_u\text{Zn}_{1-u}\text{Se}$  solid solutions were



found to conform to the model of a regular solid solution. The researchers also examined ion exchange in a stressed crystal; they made separate determinations of the elastic and dislocation components of the excess molar Gibbs energy, as well as the total excess molar Gibbs energy. The values obtained on the basis of the theoretical calculations were found to be in good agreement with published experimentally obtained values. The researchers also analyzed the profiles of the distribution of elements in Cd:ZnSe ion exchange structures obtained in one and the same melt but at different temperatures. The analysis results enabled the researchers to determine the parameters of the temperature dependence of the self-diffusion coefficients of the zinc and cadmium ions:  $D = D_0 \exp(-Q/kT)$ . For  $Zn^{2+}$ ,  $D_0 = 0.040 \text{ cm}^2/\text{s}$ , and  $Q = 1.54 \text{ eV}$ . For  $Cd^{2+}$ ,  $D_0 = 0.058 \text{ cm}^2/\text{s}$ , and  $Q = 1.73 \text{ eV}$ . Figures 5, table 1; references 23: 5 Russian, 18 Western.

#### Estimation of the Energy of Intermolecular Interactions During the Compilation of Data on Liquid Adsorption Chromatography and Spectroscopy

927M0174B Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 66 No 3, Mar 92 (manuscript received 17 Jan 91) pp 723-729

[Article by A.Z. Gamzatov, V.A. Kuznetsov, A.N. Ageyev, and Ya.I. Yashin; UDC 543.54]

[Abstract] A comparison of the results was made of a study of alkyl benzenes that was carried out by using the methods of liquid absorption chromatography and electron spectroscopy of charge-transfer complexes. The primary objective in making this comparison was to be able to obtain a quantitative estimate of the energy of nonspecific adsorbate-eluent intermolecular interaction. Electron spectra of the absorption of n-propyl-, sec-butyl-, n-butyl-, and amylbenzene charge-transfer complexes were obtained on a Hitachi-220 spectrophotometer in the range from 300 to 900 nm at room temperature. The frequency determination error did not exceed  $150 \text{ cm}^{-1}$ . The study specimens were prepared by mixing a solution of the study compounds (in a 1:1 ratio) in  $\text{CHCl}_3$  (0.5 mol/l) and a solution of tetracyanoethylene in  $\text{CHCl}_3$  (0.01 mol/l). A Tsvet-304 chromatograph with an ultraviolet detector was used to obtain the chromatograms of the polymethyl- and monoalkylbenzenes that were used as a basis for calculating the relative (to benzene) change in free energy during absorption, i.e.  $\Delta(\Delta G)$ . The column measured  $30 \times 0.6 \text{ cm}$ . KSS-4 silica gel was used as an adsorbent (specific surface,  $650 \text{ m}^2/\text{g}$ ), and n-hexane was used as an eluent. A flow velocity of  $3.6 \text{ cm/min}$  was used along with a pressure of  $10.8 \text{ MPa}$  at the column entrance; 149 seconds was required to reach a weakly absorbed substance. By combining data obtained from liquid absorption chromatography and electron spectroscopy studies, the researchers were able to separate the contributions to monoalkylbenzene retention made, on the one hand, by the volume of the adsorbate molecule (which determines the potential

energy of nonspecific interaction with the eluent and adsorbent) and, on the other hand, the spatial accessibility of these molecules to nonspecific and specific interactions with the eluent and adsorbent. The dependence of the experimentally obtained values of the relative (to benzene) changes in the free energy of adsorption from solutions in n-hexane on hydroxylated silica gel and the frequencies of the maximum of the charge transfer bands for the model alkylbenzenes studied was analyzed and found to be rather complex in nature. The qualitative conclusions that the researchers were able to draw regarding the laws of monoalkylbenzene retention enabled them to derive the following two-parameter correlation dependence:  $\delta G = -174.4 + 400.8w + 440.6E_s^0$  ( $N = 7$ ,  $R = 0.985$ ,  $s = 70 \text{ J/mol}$ ), where  $E_s^0$  represents the purely steric Palm constants that are often used in organic chemistry for the characteristic indicating the degree of screening of a reaction center by substituents and  $w$  is a parameter expressing the substituent's effective volume in relative units. The researchers concluded that the coefficients  $w$  and  $E_s^0$  in the above correlation dependence determine the sensitivity of a chromatographic system to a change in the geometric structure of a substituent in monoalkylbenzenes and that one may judge the preponderant effect of given factors on adsorbate-eluent and adsorbate-adsorbent interaction energy depending on the signs of these coefficients, their absolute values, and the relationship between them. The researchers further stated that the values of the coefficients given  $w$  and  $E_s^0$  in the aforesaid dependence provide a basis for proposing that the main manifestations of a change in the geometric structure of a substituent in a monoalkylbenzene molecule in the chromatographic system under consideration are as follows: 1) a reduction in spatial accessibility of the absorbed monoalkylbenzene molecule to molecules of n-hexane as the branching of the substituent in the latter increases and 2) an increase in the energy of nonspecific adsorbate-adsorbent interaction in the event of a transition from a less branched isomer to a more branched one. Figures 2, table 1; references 15: 12 Russian, 3 Western.

#### Partial Enthalpies and Entropies of Oxygen in Alloys of Vanadium and Niobium With Small Amounts of Transition Metals and Oxygen

927M0174C Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 66 No 3, Mar 92 (manuscript received 21 Jun 91) pp 803-806

[Article by R.F. Balabayeva, I.A. Vasilyeva, and I.S. Sukhushina, Physics Department, Yaroslavl State University; UDC 541.11]

[Abstract] The authors of this concise report have used data previously obtained by them in other studies to calculate the partial enthalpies and entropies of oxygen in alloys of vanadium and niobium with small amounts of transition metals and oxygen (i.e., solid solutions of the type  $\text{Nb}_{0.99}\text{M}_{0.01}\text{O}_{0.01}$  and  $\text{V}_{0.99}\text{M}_{0.01}\text{O}_{0.01}$ , which have yet to be studied experimentally). Partial enthalpy and entropy values were calculated for the cases of

doping with Sc, Mn, Y, Mo, Tc, La, and W in the temperature interval extending from 1,100 to 1,300 K. On the basis of the calculations performed, the researchers concluded that doping the aforementioned niobium and vanadium alloys with small amounts of Tc, Fe, W, Mn, Cr, and Mo causes an increase in partial excess Gibbs energy and thus improves their anticorrosion properties. From the standpoint of effectiveness as a way of increasing a metal's anticorrosion properties, the above alloying agents may be ranked as follows:  $\text{Mo} < \text{Mn}(\text{Cr}) < \text{Fe}(\text{W}) < \text{Tc}$ . In the case of  $\text{V}_{0.99}\text{M}_{0.01}\text{O}_{0.01}$  alloys, the corresponding ranked series would be as follows:  $\text{Nb}(\text{Ta}) < \text{Mo} < \text{Mn}(\text{Cr}) < \text{Fe}(\text{W}) < \text{Tc}$ . Figure 1, tables 2; references 4: 1 Russian, 3 Western.

#### Superheating of a Crystal

927M0174D Moscow ZHURNAL FIZICHESKOY  
KHIMII in Russian Vol 66 No 3, Mar 92 (manuscript  
received 23 Jan 91) pp 819-821

[Article by M.N. Magomedov, Dagestan Affiliate, Geothermy Problems Institute, Russian Academy of Sciences, Makhachakala; UDC 536.421:546.293]

[Abstract] It is a well-known fact that a liquid phase may be easily supercooled by slow cooling below the melting point, whereas the same crystals can only be superheated at high heating rates (about  $10^8$  K/s). No currently existing theoretical models can explain the physical nature of this asymmetry of the crystal-liquid phase transition. In an effort to account for this asymmetry, the author of this concise report calculated the temperature dependences of spinodals of a crystal and liquid and their melting lines for macro- and microsystems. For the sake of concreteness, the author centered his calculations around a face-centered argon crystal. The author conducts his analysis for the case of M-systems, which is to say systems in which the number of particles ( $N$ ) is infinite (i.e.,  $N = \infty$ ). He then proceeds to demonstrate that at low pressures the values of the temperature instability of both the crystal and liquid on the isobar decrease as the number of particles ( $N$ ) increases just as the equilibrium-melting temperature does. At low pressures, it is comparatively easy for a liquid to be supercooled, but superheating of a crystal is very difficult. The inverse asymmetry is observed to be true at high pressures: It is comparatively easy for a crystal to be superheated, whereas a liquid may only be supercooled at high rates of cooling. Two publications are cited as presenting experimental confirmation of this finding. The author concludes by saying that the asymmetry of the face-centered crystal-to-liquid asymmetry transition relative to superheating and supercooling is the result of a more general face-centered crystal-liquid symmetry that may be observed by studying the superheating and supercooling of crystals at arbitrary pressures. Figure 1; references 13: 12 Russian, 1 Western.

#### Computing the Volume and Coefficient of Bulk Expansion in a Model Crystal and in Glass Having Vacancies Modified by Molecular Dynamics

927M01751 Moscow ZHURNAL FIZICHESKOY  
KHIMII in Russian Vol 66, No 4, Apr 92 (manuscript  
received 24 Apr 91) pp 1088-1091

[Article by A. K. Ashurov, A. K. Nasrulloev, and O. K. Khalilov; UDC 536.4211]

[Abstract] The modified method of molecular dynamics makes it possible to compute the thermodynamic and spectral characteristics of a system over a wide range of temperature, pressure, and number of particles in the base nucleus. Calculation of the volume occupied by a single particle as a function of the concentration of vacancies is of great interest in respect to crystal models and glass. A vacancy is understood to mean the absence of particles in the nodes of the granicentric cubic lattice of the initial molecule. In the present work the modified method of molecular dynamics was used to compute the coefficient of bulk expansion in a model crystal and in glass having vacancies. Glass-crystal and glass-liquid phase transitions as well as phase erosion were detected. The change in volume of a model crystal and glass for a single particle in relation to the volume corresponding to a unit of vacancy concentration was analyzed. Figures 2; references 7: 6 Russian, 1 Western.

#### The Spectrum of One-Time Energy Losses of Electrons of Polycrystalline Fullerene $\text{C}_{60}$

927M0177A St. Petersburg PISMA V ZHURNAL  
TEKHNICHESKOY FIZIKI in Russian Vol 18 No 11,  
Jun 92 (manuscript received 4 Apr 92) pp 19-22

[Article by V.I. Rubtsov and Yu.M. Shulga]

[Abstract] The authors of the study reported herein worked to obtain a spectrum of the one-time electron energy losses for polycrystalline  $\text{C}_{60}$  that could be compared with the loss function derived from independent experiments or theoretical calculations of the electron structure of  $\text{C}_{60}$ . The  $\text{C}_{60}$  used during the study was synthesized and purified as described elsewhere. A polycrystalline coating containing at least 99%  $\text{C}_{60}$  was applied onto an aluminum substrate. The effective thickness of the coating applied was between 0.1 and 0.9  $\mu\text{m}$ . For the sake of comparison, the loss spectra of graphitic specimens that had been prepared by molding polycrystalline powders were also measured. An RNI-551 spectrometer equipped with a double cylindrical mirror-type analyzer with an attachment for angular measurements and with a coaxial electron gun analyzer was used to measure the electron spectra. The beam of primary electrons had an energy of 2,000 eV and an energy distribution half-width of 0.5 eV. The primary electrons had an angle of incidence of  $42^\circ$  relative to the outer normal to the surface. The pressure of the residual gases in the measurement chamber did not exceed  $3 \times 10^{-10}$  torr. The measurements taken were corrected for the

dependence of the analyzer's transmissivity on the kinetic energy of the electrons being analyzed. The loss and one-time loss spectra of both the graphite and  $C_{60}$  were found to contain two primary maximum that were caused by the excitation of the plasma oscillations of all of the valence electrons and the  $\pi$ -subsystem alone. The maxima of the spectrum for  $C_{60}$  were at 25.2 and 5.6 eV, whereas those for the graphite were at 26.6 and 6.6 eV. The positions of the maxima for the graphite were consistent with data reported in the literature. The values obtained for  $C_{60}$  were close to those obtained in experiments on the passage of high-energy (100 to 200 keV) electrons through thin layers of  $C_{60}$  but different from values obtained in a study of the spectrum of reflected electrons and the satellite structure of x-ray photoelectron spectra of Cis. The difference between the spectra of one-time losses of  $C_{60}$  from those of graphite extend beyond the shift in their main maxima to the side of lower losses. The losses observed between the main maximum in the case of  $C_{60}$  are also observed to have a higher intensity, which is in agreement with published theoretical calculations of the electromagnetic response function for a  $C_{60}$  cluster. Other less intense distinctions may also be identified in the spectrum of the one-time losses of  $C_{60}$ . Figure 1; references 17: 3 Russian, 14 Western.

#### Novel Rubidium and Cesium Fluorozirconates and Fluorohafnates

927M0188B Moscow KOORDINATSIONNAYA  
KHIMIYA in Russian Vol 18 No 1, Jan 92 (manuscript  
received 22 Aug 91) pp 48-55

[Article by R. L. Davidovich, V. B. Logvinova, L. V. Teplukhina, Institute of Chemistry, Far Eastern Department, USSR Academy of Sciences]

UDC 541.49:54666.83'161

[Abstract] In an attempt to determine reaction conditions for the synthesis of rubidium and cesium pentafluorozirconates and pentafluorohafnates with the composition  $MAF_5 \cdot H_2O$  (where M= Rb, Cs and A= Zr, Hf) and to analyze the composition of these compounds with  $Rb^+$  and  $Cs^+$  cations which form with low molar ratios of the starting components, systematic investigation of the reaction of MF or MCl with  $(H_3O)_2ZrF_6$  or  $(H_3O)_2HfF_6$  was carried out in aqueous solution, using a wide range of molar ratios of the components. Several novel fluorozirconates and fluorohafnates were synthesized:  $Rb_3Zr_4F_{21} \cdot H_2O$ ,  $Cs_3Zr_4F_{21} \cdot 3H_2O$ ,  $Rb_3Hf_4F_{21} \cdot 3H_2O$  and  $Cs_3Hf_4F_{21} \cdot 4H_2O$ . The composition of the end products depended on the molar ratio of the reagents and on the alkali metal halides used. Analysis of the x-ray, IR spectroscopic and thermogravimetric analysis data

showed that the compounds described in literature as  $Rb(Cs)ZrF_5 \cdot H_2O$  and  $RbHfF_5 \cdot H_2O$  are actually  $M_3A_4F_{21} \cdot 3H_2O$  and  $Cs_3Hf_4F_{21} \cdot 4H_2O$ , the composition of which was determined in this work for the first time. Obviously proper corrections should be made in the atlas of the IR spectra and X-ray data. Tables 3; figures 2; references 12: 10 Russian, 2 Western.

#### Thermochemistry of Cobalt (II) Monothiolate Complexes in Aqueous Solution

927M0188C Moscow KOORDINATSIONNAYA  
KHIMIYA in Russian Vol 18 No 1, Jan 92 (manuscript  
received 8 Jul 91) pp 83-85

[Article by D. Kh. Kamysbayev, R. N. Utegulov, Kh. K. Ospanov, Kazakh State University imeni S. M. Kirov; UDC 536:541.49]

[Abstract] Cobalt (II) forms a complex with 2,3- dimer-captopropene sulfonate ion ( $Un$ ) with a composition of  $CoUn^+$  and  $CoUn_2^+$ . Investigation of these complexes was carried out with potentiometric and colorimetric methods yielding thermodynamic characteristics of their formation. On the basis of the data obtained at 298 K it was concluded that a conversion of the 1:1 complex to a 1:2 complex resulted in an increase of  $\Delta H$ , showing a greater bond strength of the 1:2 complex. This complex exists as a five member chelate cycle. Tables 2; references: 6 (Russian).

#### Coordination Compounds of Rare Earth Elements With Salicyl Aldehyde Semicarbazone

927M0188E Moscow KOORDINATSIONNAYA  
KHIMIYA in Russian Vol 18 No 1, Jan 92 (manuscript  
received 28 Dec 90) pp 107-111

[Article by N. M. Samus, M. V. Gandziy, I. V. Sinitsa, V. I. Tsapkov, Moldova State University; UDC 541.49:546.65:547.491.1:547.576]

[Abstract] The goal of this work was to synthesize coordination compounds of rare earth elements ( $Ln = La, Y, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb$ ) with salicyl aldehyde semicarbazone. These complexes were obtained by reacting  $L(NO_3)_3 \cdot 6H_2O$  in ethanol with salicyl aldehyde semicarbazone and 25% aqueous ammonia until pH 9 was reached; then the mixture was heated to solution and cooled to precipitate the product. Depending on the ratio of reactive components and reaction conditions, the following products were obtained:  $Ln(HL)_3 \cdot nH_2O$  ( $n = 1, 2, 3$ ) or  $Ln(HL)L \cdot mH_2O$  ( $m = 2, 3, 4$ ). Kinetic parameters of the dehydration of  $Ln(HL)L \cdot 2H_2O$  increased in the order:  $Tb < Dy \leq Ho < Er < Yb < Y$ . On the basis of physical-chemical studies, a combination structure for these products was proposed. Tables 3; references 10: 7 Russian, 3 Western.



**Spectral Manifestation of Fractal Distribution of Molecules Adsorbed in Pores Under Conditions of Heterogeneous Intermolecular Reactions**

927M0189A Moscow ZHURNAL FIZICHESKOY  
KHIMII in Russian Vol 66 No 2, Feb 92 pp 329-334

[Article by A. V. Sechkarev, V. I. Zemskiy, V. N. Beger, Yu. L. Kolesnikov; UDC 541.183]

[Abstract] Spatial distribution of adsorbed molecules determines the characteristics of many processes occurring on the surface. Fractal distribution is characterized by the observation that the number of particles  $n(R)$  found within the sphere with a radius  $R$  around any randomly selected particle increases as  $n(R) \approx R^7$ , in contrast to an even distribution when  $n(R) \approx R^3$ . In case of real physical objects, the fractal type distribution occurs only within a definite range of dimensions, disappearing when the distance between the particles is too large or too small. Fractal distribution of adsorbed molecules has not been adequately studied. In the present work it was shown that in case of small concentrations of adsorbed molecules, their distribution will be determined not by their interaction with each other but by interaction with the adsorbent. Concentration relationships of the extinguishment and depolarization of the fluorescence of adsorbed dye molecules were explained by non-radiating energy transfer of the electronic excitation between the molecules using the hypothesis of fractal distribution of such molecules throughout the volume of the adsorbent. Figures 3; references 15: 11 Russian (1 by Western author), 4 Western.

**Characteristics of Fractal Structure of Polymer Molecules and Equation of Polymer in Molten State**

927M0189B Moscow ZHURNAL FIZICHESKOY  
KHIMII in Russian Vol 66 No 2, Feb 92 pp 335-337

[Article by V. M. Sysoyev; UDC 541.64:536;6]

[Abstract] Isothermal compression of polymer systems in a wide range of pressures is described well by Tait (Spelling not certain - abstractor) equation. Effective constants of the potential of intermolecular interactions were estimated starting from the preposition about the fractal structure of the polymer lump viewed as a variety of random dimensions in a real three dimensional space. Comparative analysis of the equations describing the states of molten polymer and low molecular fluids makes it possible to evaluate the index  $\nu$ , i.e. to get information on fractal structure of the polymer molecule. For example, analysis of the state of polystyrene at high pressures, when polymers undergo solidification, shows that the  $Z$  value decreases to 0.1, corresponding to a transition from  $\nu = 3/5$  to  $\nu = 1/2$ , that is to the state at which the polymer lumps appear to be ideal. References 10: 7 Russian (2 by Western authors), 3 Western.

**Diffusion-Limited Aggregation of Aqueous-Salt Solution of Albumen in Thin Films Over Solid Support. Experiment and Computer Model**

927M0189C Moscow ZHURNAL FIZICHESKOY  
KHIMII in Russian Vol 66 No 2, Feb 92 pp 352-355

[Article by R. I. Mints, S. A. Skopinov, R. M. Kadushnikov, D. B. Berg, Ural Polytechnical Institute imeni S. M. Kirov, Russian Academy of Sciences; Ural Department of Scientific-Engineering Center of Ecological Safety, Yekaterinburg; UDC 538.975]

[Abstract] In this work the principal characteristics of the albumen aggregation process in an aqueous-salt solution were examined comparing the experimental results with those obtained from computer simulations. It was shown that in absence of albumen, pyramidal NaCl crystals formed on the support film. With increasing concentration of albumen, skeletal forms began to appear leading to dendritic structures with characteristic morphology. Analysis of these data and comparison with computer generated material supported the idea that the morphology of these structures resulted from phase stratification processes of the salt and albumen components. The principal controlling parameter of this process at a given temperature was the initial concentration of two crystallizing components. This makes it a convenient physical model for studying general physical laws of two-dimensional aggregations. Figures 2; references 13: 2 Russian, 11 Western.

**Expansion of Intermolecular Spectrum Bands of Combined Diffraction of Fractal Clusters of Polycrystals in Porous Glass**

927M0189D Moscow ZHURNAL FIZICHESKOY  
KHIMII in Russian Vol 66 No 2, Feb 92 pp 356-358

[Article by A. V. Sechkarev, V. N. Beger, Yu. A. Fadeyev; UDC 541.183]

[Abstract] Spectra of lattice vibrations of a number of crystals inserted into a silicate matrix with an average pore size of about 8nm were studied. A broadening and a shift of the lines of combined diffraction spectrum was observed at low frequencies in comparison to the polycrystalline spectrum. In an attempt to explain this phenomenon, the hypothesis of fractal structure of porous glasses was used. A formula was developed by which a three-fold enlargement of the spectral half-width was to be expected; indeed, experimental data confirmed these calculations. Figure 1; references 7: 6 Russian, 1 Western.

**Free Volume in Mesogene Crystals. Comparison of Results of Annihilation of Positron Methods With X-ray Structural Analysis**

927M0189E Moscow ZHURNAL FIZICHESKOY  
KHIMII in Russian Vol 66 No 2, Feb 92 pp 406-410

[Article by Ye. A. Kopelyan, S. A. Skopinov, A. P. Polishchuk, S. V. Sereda, Ural Polytechnical Institute;

Center of Ecological Safety, Ural Department of Russian Academy of Sciences, Yekaterinburg; Institute of Physics, Ukrainian Academy of Sciences, Kiev; UDC 539.26]

[Abstract] The method of electron-proton annihilation (EPA) has been used for decades to study various molecular systems; EPA yields unique information on the local structure and dynamic processes of short duration in ordered, partially ordered and in the non-ordered molecular media. Members of a homologous series of toluidines were studied by the EPA and x-ray structural analysis methods in an attempt to discover any relationship between the annihilation spectra parameters and the characteristic of local molecular structure and of the free volume of the (CO) medium. Spectra of toluidine positron life time (PLT) were determined as a function of temperature. The spectra of angle correlation of the annihilating radiation (ACAR) were determined in solid phase. An even-odd effect in the toluidine spectra of the PLT and ACAR was observed in solid phase. A model of free volume was proposed in an attempt to interpret the data. According to this model, the extent to which the form of elementary free volume deviated from the spherical shape was greater in the even homologues than in the odd ones. Molecule packing and topology of free volume in the elemental cells of the monocrystals was determined from the x-ray structural data. It was concluded that data on the free volume obtained from annihilation experiments in molecular crystals correspond to accurate x-ray structural data. With corresponding normalization of the annihilation parameters, the method yields accurate information about microstructure reconstruction in condensed molecular medium. Table 1; figures 5; references 9: 5 Russian, 4 Western (1 by Russian authors).

#### **Dielectric Relaxation Phenomena in Complex Liquid Crystal Esters With Central Polymethylene Groups**

927M0189F Moscow *ZHURNAL FIZICHESKOY KHIMII in Russian* Vol 66 No 2, Feb 92 (manuscript received 21 Dec 90) pp 478-482

[Article by Ye. I. Ryumtsev, A. P. Kovshik, D. A. Ragimov, L. A. Karamysheva, Scientific Research Institute of Physics, St. Petersburg State University; UDC 548.0:532.783]

[Abstract] Molecular characteristics and macroscopic dielectric properties of 4-cyanodiphenyl esters of  $\omega$ -(4-trans-alkylphenyl)- and  $\omega$ -(4-trans-alkylcyclohexyl)-carboxylic acids are reported. Results were obtained for their solutions, the isotropic phase and the liquid crystalline state. From these data analysis of the dipole structure of these compounds in various phases were carried out. Quantitative analysis, the authors pointed out, requires consideration of the degree of temperature separation of the substance from the transition point of the respective sample from the isotropic to liquid crystalline state along with its elasticity modulus, rotational viscosity, and a detailed analysis of possible mechanisms

of the rotation of molecules around the perpendicular axis. It was shown that in the mesophase the low frequency dispersion region of the parallel component of the dielectric permeability depends on the length of the central polymethylene chain. Tables 2; figures 2; references 7: 5 Russian, 2 Western (1 by Russian authors).

#### **Method for Evaluating Properties of Catalysts Based on Registration of Acoustic Emission Signals**

927M0189G Moscow *ZHURNAL FIZICHESKOY KHIMII in Russian* Vol 66 No 2, Feb 92 (manuscript received 15 May 91) pp 576-577

[Article by A. A. Pimonov, Yu. I. Solovetskiy, Department of Chemistry, Moscow State University imeni M.V. Lomonosov; Belgrade, Technological Institute of Construction Materials imeni I. A. Grishmanov; UDC 541.128:628.179.16]

[Abstract] At present there are no practical instrumental methods for a rapid determination of the duration of catalyst runs and of the related macrostructural changes (development of macropores, relocation of macrocrystals, pore filling with reaction products, possible local overheating of the catalyst, etc.). With this in mind, the authors investigated the properties of the granules of industrial Klaus process catalysts using the method of acoustic emission (AE). Any change in the structure of a solid body (phase transition, formation of dissipative structures during external load, transfer of dislocation groups through phase borders or relocation to the surface) is accompanied with energy emission during  $10^{-6}$  s, resulting in appearance of short impulses, the AE, in the ultrasound range (0.1-1.0 MHz). It was shown that the AE method may be used for estimating the duration of the catalyst run and the temperature regimens of the process with a parallel estimation of the strength characteristics of heterogeneous catalysts. Figure 1; references: 2 (Russian).

#### **Sulfur Ilides. Report 5. Reaction of Phthalimide-Containing Keto-Stabilizing Sulfonium Ilides**

927M0193C Moscow *IZVESTIYA AKADEMII NAUK ROSSIYSKOY AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian* No 3, Mar 92 (manuscript received 5 Mar 91) pp 720-726

[Article by S. N. Lakeyev, F. Z. Galin, L. M. Khalilov, and G. A. Tolstikov, Chemistry Institute, Ufa; UDC 547.759:547.94]

[Abstract] A series of new keto-stabilizing sulfonium ilides were synthesized from amino acids in a previous work. In the present work the properties of these ilides were studied on the basis of phthalimide-containing sulfur ilide keto-stabilizers. In addition to the formation of products customary for sulfur ilide keto-stabilization, a rearrangement takes place in the reaction with acrylonitrile resulting in formation of 1,1-disubstituted cyclopropanes.



**Manifestation of the Effect of Phosphorus-Containing Groupings in the  $^{13}\text{C}$  NMR Spectra of *para*-Phosphorylated Dimethylanilines**

927M0178A St. Petersburg ZHURNAL OBSHCHEY  
KHIMII in Russian Vol 61 (123) No 12, Dec 91  
(manuscript received 10 Aug 90) pp 2665-2669

[Article by G.V. Ratovskiy, S.L. Belaya, L.M. Sergiyenko, V.I. Donskikh, and A.A. Tolmachev; UDC 547.241:543.42]

[Abstract] The manifestation of the effect of phosphorus-containing groupings in the  $^{13}\text{C}$  NMR spectra of a series of *para*-phosphorylated dimethylanilines was examined. The dependence of the chemical shifts ( $\delta_{\text{C}}$ ) of the carbon atoms of the benzene ring on the inductive and resonance effect of the phosphorus-containing groupings  $\text{PX}_2$ ,  $\text{P(Y)X}_2$ ,  $\text{PL}_2\text{XCl}$  (where  $\text{X} = \text{Me}$ ,  $\text{Et}$ ,  $\text{OEt}$ ,  $\text{NH}_2$ ,  $\text{NMe}_2$ ,  $\text{NEt}_2$ , and  $\text{Cl}$ ;  $\text{Y} = \text{O}$ ,  $\text{S}$ , and  $\text{NH}$ ; and  $\text{L} = \text{NEt}_2$ ) was examined. A Bruker WP-200 spectrometer operating at a frequency of 50.3 MHz was used to record the  $^{13}\text{C}$  NMR spectra of the 19 study compounds in dichloroethane. The chemical shifts of the  $^{13}\text{C}$  nuclei were measured relative to the central peak of dichloroethane (51.7 ppm). The measurement error amounted to 0.02 ppm. M-80 and Perkin-Elmer-557 IR spectrometers were used to record the IR spectra of the study compounds in a medium of cyclohexane or dioxane depending on the given compound's solubility. The method of direct integration was used to find the integral intensities. The measurement error amounted to 7%. The analyses performed established that as  $\text{X}$  is varied, the  $\pi$ -acceptor effect of the said groupings increases in the series  $\text{NAlk}_2 < \text{Alk} < \text{OAlk} \ll \text{Cl}$ . In the case of phosphorus-chlorine groupings, a competing effect of the ligand attenuating the  $\sigma, \pi$ -conjugation of the  $\text{PX}_2$  and  $\text{C}_6\text{H}_4\text{NMe}_2$  fragments was also observed. The discrepancies between the parameters obtained from the  $^{13}\text{C}$  NMR and those obtained from the IR spectroscopy studies were explained. Table 1; references 5: 4 Russian, 1 Western.

**The Photoelectron Spectra and Electron Structure of Organophosphorus Compounds. XIII. (1-Dialkylaminoalkylidene)phenylphosphines**

927M0178C St. Petersburg ZHURNAL OBSHCHEY  
KHIMII in Russian Vol 61 (123) No 12, Dec 91  
(manuscript received 18 Jun 90) pp 26-84

[Article by V.V. Zverev and A.S. Ionkin, Organic and Physical Chemistry Institute imeni A.Ye. Arbuzov, Kazan Scientific Center, USSR Academy of Sciences; UDC 541.6]

[Abstract] Photoelectron spectroscopy and quantum chemistry techniques were used to investigate the photoelectron spectra and electron structure of three compounds: (dimethylaminomethylene)phenylphosphine, 1-dimethylaminoethylidene)phenylphosphine, and 1-pyrrolidinylmethylene)phenylphosphine. The three study phosphalkenes were synthesized as published

elsewhere. An ES-3201 spectrometer was used with He(I) resonance radiation to record the photoelectron spectra, and the energy scale was calibrated on the basis of argon lines. The spectral measurements were then compared with the results of a nonempirical calculation of phosphalkene with an STO 3G basis with partial optimization of its geometry. In accordance with the quantum chemical calculations performed for a (dimethylaminomethylene)phenylphosphine molecule, its total energy is at a minimum when the benzene ring is turned by an angle of about  $30^\circ$ . The rotation of this radical around the C-P bond was found to be reflected only slightly in the magnitudes of the charges on the atoms and the energy of the occupied orbitals but to cause significant changes in the energies of the free orbitals. The displacement of the charge from the nitrogen atom to the phosphorus atom in (dialkylaminoalkylidene)phenylphosphines that was discovered was attributed to  $\pi$ - $\pi$ -interaction, affected all of the atoms of the molecules, and caused the destabilization of the highest occupied molecular orbital at 1.50 eV. Figures 4, table 1; references 9: 5 Russian, 4 Western.

**The Photoelectron Spectra and Electron Structure of Organophosphorus Compounds. XIV. 1,3,2-Diazaphospholenes**

927M0178D St. Petersburg ZHURNAL OBSHCHEY  
KHIMII in Russian Vol 61 (123) No 12, Dec 91  
(manuscript received 21 Jan 91) pp 2690-2692

[Article by V.V. Zverev, T.V. Gryaznova, and A.M. Kibardin, Organic and Physical Chemistry Institute imeni A.Ye. Arbuzov, Kazan Scientific Center, Academy of Sciences; UDC 541.6:547.1'118]

[Abstract] 1,3,2-Diazaphospholenes are new heterocyclic compounds that have been not yet been studied in any great detail. In view of this fact, the authors of the study reported herein investigated the photoelectron spectra of seven different 1,3,2-diazaphospholenes. Specifically, they studied four different 2-R-1,3-dibutyl-4,5-dimethyl-1,3,2-diazaphosphol-4-enes, two different 2-R-2-oxo-1,3-dibutyl-4,5-dimethyl-1,3,2-diazaphosphol-4-enes, and 2,4-dichloro-1,3-dicyclohexyl-1,3,2-diazaphosphol-2-ene. The seven 1,3,2-diazaphospholenes studied were synthesized as described elsewhere. An ES-3201 spectrometer with an He(I) resonance source was used to record the photoelectron spectra of the study 1,3,2-diazaphospholenes. The studies performed established that 1,3,2-diazaphospholenes are characterized by primary ionization potentials with low values. The spectra of the study phospholenes contain resolved bands only in the ionization energy range up to 10.2 eV. The subsequent portion of their spectrum represents an intensive wide band that is dictated largely by direct ionization of the butyl-group orbitals (butane has an ionization potential of 10.5 eV). The four highest occupied molecular orbitals of 1,3,2-diazaphospholenes are formed by a linear combination of orbitals of undivided nitrogen, phosphorus, and  $\pi$ -bond pairs. The fact that the highest occupied  $n$ - $\pi$ -type

molecular orbital has an energy that is very different from the energy of the next orbital (a difference of 1.7 eV) points to intensive  $n-\pi$  interaction. The undivided phosphorus pair is shown to make only an insignificant contribution to the highest occupied molecular orbital. Figures 2, table 1; references 10: 7 Russian, 3 Western.

**The Reaction of Nitrophenol Salts With Cyclic Phosphonitryl Chlorides in Low-Polarity Organic Media**

927M0178E St. Petersburg ZHURNAL OBSHCHEY  
KHIMII in Russian Vol 61 (123) No 12, Dec 91  
(manuscript received 26 Jul 90) pp 2693-2697

[Article by A.Ye. Shumeyko, A.A. Afonkin, A.F. Popov, Zh.P. Piskunova, A.A. Yakovets, and S.A. Grebenyuk, Physical and Organic Chemistry and Coal Chemistry Institute, Ukraine Academy of Sciences, Donetsk; UDC 547.564-546.13.17.18]

[Abstract] The authors of the study synthesized analogues of the active form of the interface catalyst  $X-PhO^+Q^-$  [where  $X = 4-NO_2$  (salt 1), 2,5-( $NO_2$ )<sub>2</sub> (salt 2), and 2,4-( $N$ )<sub>2</sub> (salt 3);  $Q = Et_3BzN$  (a),  $Bu_4N$  (b), or  $K(18-crown-6)$  (c)] as described elsewhere. They then

proceeded to determine the reactivity of the said nitrophenol salts at 298 K in a model reaction in chlorobenzene, o-dichlorobenzene, and mixtures thereof. The study reactions all occurred quantitatively and irreversibly. The phenolysis rate of salt 3 was measured on a VSU-2P spectrometer, while that of salts 1 and 2 was measured by an SP-176 high-speed spectrometer equipped with a stopped-stream unit. The studies performed established that in low-polarity organic media, tetraalkylammonium nitrophenolates enter into a bimolecular nucleophilic substitution with cyclic phosphonitryl chlorides in the presence of ions and ionic pairs whose individual reactivities depend on the size of the substrate cycle, the basicity of the anion, the size of the ionic pair's cation, and the dielectric constant of the medium. Specifically, the phenolysis rate was found to increase as the basicity of the nitrophenolate ion increased. Higher-polarity solvents were also found to increase the phenolysis rate. The observed pseudo-first-order rate constants remained constant within the confines of 2 to 3 percentage points throughout the course of the process and could be reproduced with a precision up to 5%. Figures 2, table 1; references 8 (Russian).

**Estimating the Effect of Heavy Metals on Agrolandscape Soils' Ability To Cleanse Themselves of Residual Quantities of Stable Pesticides**

927M0171A Moscow AGROKHIMIYA in Russian No 3, Mar 92 (manuscript received 18 Jul 91) pp 67-74

[Article by R.V. Galiulin, V.P. Uchvatov, Soil Science and Photosynthesis Institute, USSR Academy of Sciences, Pushchino, Moscow Oblast; UDC 632.95.028:631.416.9]

[Abstract] The author of this study first made a determination of the heavy metal content of Azerbaijan's farming lands and then worked to find correlations between the concentrations of heavy metals and stable organochlorine pesticides present in the soil. Specifically, they analyzed soil sampled from six different areas to determine their individual and total concentrations of the following heavy metals: Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb. Samples taken from soil layers 0 to 25 and 0 to 120 cm deep were analyzed. The average concentrations of Cu, Zn, Ni, and Co were found to be severalfold higher than their abundance ratio, while that of Cr, Mn, Fe, Cd, and Pb were either below or slightly below their abundance ratio. Isolated instances of higher- or lower-than-anticipated amounts of individual heavy metals were found in several of the individual regions of Azerbaijan studied. Next, the researchers analyzed their findings in an attempt to spot correlations between the concentrations of heavy metals and stable organochlorine pesticides (i.e., the sum of the isomers hexachlorocyclohexane [HCCH], dichlorodiphenyltrichloromethylmethane [DDT], and its degradation products dichlorodiphenyldichloroethylene [DDE] and dichlorodiphenyldichloroethane [DDD] and the ratio DDE/DDT). The correlation analysis performed established a positive correlation between the Cr content and the sum of the HCCH isomers in study region 3, which is to say that the higher the Cr concentration, the more pesticide is absorbed. A strong positive correlation was also established in study region 6 between the concentration of Cr and the sum of the isomers of HCCH ( $\Sigma$  HCCH) and the sum of the organochlorine pesticide isomers. The DDE/DDT ratio in the study specimens was examined as a marker of the initial stage of the soil's cleansing itself of DDT (i.e., beginning of the transformation of DDT to its oxidation dehalogenation product DDE). The positive value of the correlation factor found was confirmation that the higher the Cr concentration the higher the DDE/DDT ratio. This correlation was taken as an indirect indication of the catalytic effect of Cr on the process of the chemical transformation of DDT. Of all the heavy metals studied, Fe was found to manifest the highest correlation with total HCCH isomers and total organochlorine pesticide isomers for four of the individual regions and for the entire study area. Overall, the researchers concluded that the behavior of organochlorine pesticides in the soils of the study region should be dictated primarily by the presence of Fe and Mn. From the standpoint of significance of the correlation of their

concentration with residual quantities of stable organochlorine pesticides, the heavy metals studied may be ranked as follows: Fe /g Mn /g Cr /g Ni = Cu /g Co = Cd = Pb. Tables 2; references 12: 9 Russian, 3 Western.

**Immunochemical Analysis and Its Use To Determine Residual Quantities of Pesticides**

927M0171 Moscow AGROKHIMIYA in Russian No 3, Mar 92 pp 110-122

[Article by A.V. Chigrin, Krasnodarskaya Kray Plant Protection Station, Krasnodar; UDC 543:632.95]

[Abstract] The first attempt to summarize information regarding the use of immunochemical analysis in determining residual quantities of pesticides was made in 1990 by Zhenchuzhin and Gorbets. Their review did not cover the main principles and stages of the conduct of immunochemical analysis. For this reason, the author of the present review has set his goal as acquainting specialists in the field of analytic chemistry with the basic principles and methods of immunochemical analysis of pesticides. First, he outlines the development of immunochemical analysis. Next, he defines five key concepts of immunochemical analysis. The main methods of conducting an immunochemical analysis are analyzed. Three basic approaches are covered: 1) competition between tagged and nontagged hapten for the binding centers of solid phase-immobilized specific antibodies; 2) competition of immobilized and free hapten for the binding centers of specific enzyme-tagged antibodies; and 3) use of tagged enzymes of secondary antibodies in reactions. The main merits of using immunochemical analysis to determine residual quantities of pesticides are stated as follows: 1) high sensitivity that is at least on a par with the sensitivity of physicochemical methods; 2) high specificity; 3) high speed; 4) low cost; 5) the possibility of using extracts that have either not been purified or only minimally purified (as opposed to the multistaged purification required with physicochemical methods); 6) the lack of any need for derivative analysis of the substance being analyzed; and 7) high productivity. The disadvantages of immunochemical analysis for determination of residual quantities of pesticides are stated as follows: 1) too high a specificity, which creates problems in adapting immunochemical analysis for determination of residual quantities of pesticides in multicomponent specimens; 2) the presence of a nonspecific inhibition of immune response and cross reactions that affect the precision of the analysis results even when the specimen being analyzed does not contain multiple components; 3) the need to use reagents that are not yet commercially available; 4) the exceptional high requirements imposed with respect to the purity of all vessels and equipment; and 5) the novelty of the approach itself, which creates problems when nonspecialists attempt to master the method. The reviewer concludes with a call for the centralized production of sets of immunoreagents and the development of facilities to produce the equipment

required for immunochemical analysis in the former Soviet Union. Figures 3, table 1; references 117: 25 Russian, 92 Western.

**High-Performance Liquid Chromatography—Promising Method for Determining Residual Quantities of Pesticides**

927M0176F Moscow AGROKHIMIYA in Russian  
No 1, Jan 92 pp 139-150

[Article by M.A. Klisenko and T.L. Makarchuk; UDC 632.95:543.54]

[Abstract] The prospects of high-performance liquid chromatography as a method of determining residual quantities of pesticides were examined. The development of high-performance liquid chromatography from its beginnings in the mid-sixties was traced. The various detectors, including electrochemical and refractometric detectors, used in the high-performance liquid chromatography of pesticides are discussed. The various sorbents, eluents, and equipment used are also covered along with the procedures used to prepare samples for high-performance liquid chromatography analysis. The second half of the review consists of separate sections examining the high-performance liquid chromatography analysis of organochlorine, organophosphorus, and other pesticides. On the basis of the information presented, the authors conclude that chromatographic analysis methods are being widely used to monitor residual quantities of pesticides. They demonstrate that high-performance liquid chromatography offers a number of advantages over other chromatography techniques and especially over gas-liquid chromatography. The main advantage of high-performance liquid chromatography is said to be that it permits the determination of thermally unstable preparations (carbamates) and that it allows investigators to determine synthetic pyrethroids at a single wavelength whereas gas chromatography requires the use of two detectors. The facts that high-performance liquid chromatography allows for direct input of samples and that it permits the isolation of enantiomers are also noted. High-performance liquid chromatography is also deemed promising for use in studying pesticide decomposition products such as phenols and dimethyldithiophosphoric acids and is said to have greatly expanded the spectrum of pesticide determination thanks to the fact that it may be used in both reverse-phase and forward versions (both of which permit on-line purification). Because detector sensitivity and selectivity remain important problems with respect to further advances in high-performance liquid chromatography, further research is needed in the areas of development of new high-performance and selective detectors, automated sample preparation and analysis equipment, and robotics. Table 1; references 192: 15 Russian, 177 Western.

**Analysis of Residual Quantities of Pesticides by the Method of Liquid Chromatography**

927M0176G Moscow AGROKHIMIYA in Russian  
No 1, Jan 92 pp 169-176

[Article by I.I. Miroshnichenko and L.G. Kretova, Central Institute for the Agrochemical Service of Agriculture; UDC 632.95:543.544]

[Abstract] Gas-liquid chromatography with the use of packed and capillary columns is the leading method of pesticide analysis. Many pesticides cannot be determined by using gas-liquid chromatography owing to their instability at high temperatures, their weak volatility, or the inadequate sensitivity of element-specific detectors. Conventional investigation of such compounds by the method of plane thin-layer chromatography permits the determination of pesticides in concentrations as low as tenths of a milligram per kilogram, which is hardly sufficient from the standpoint of analyzing residual quantities of toxic chemicals. High-performance liquid chromatography, on the other hand, makes it possible to determine residual quantities of both pesticides and their decomposition products. Recent advances in the field of high-performance liquid chromatography include the development and use of electron-capture, fluorimetric (the most widely used type of detector in pesticide analysis), electrochemical, and photoinductive detectors. As detectors and detection techniques become increasingly more sensitive, the purity of specimens for use with high-performance liquid chromatography has also become increasingly critical. Methods have been developed for extracting aqueous specimens by using ion-exchange columns, columns with reverse phases, and carbon cartridges. The authors of this review have compiled a 3-page table outlining the conditions for determining the individual substances belonging to the following categories by means of high-performance liquid chromatography: carbamates, urea derivatives, sulfonyl ureas, triazines, phenoxy herbicides, chlorobenzoic acid derivatives, dinitroaniline derivatives, phosphorus-containing compounds, fluorine-containing compounds, heterocyclic compounds, pyridine derivatives, cyclohexanone derivatives, pyrethroids, and fungicides. The type of column, mobile phase, and detector required for the determination of each substance covered is listed alongside that substance together with the citation of a source in which the given procedure is detailed. Table 1; references 73: 4 Russian, 69 Western.

**Phosphorylmethyl-N-(1-Hydroxy-2,2,2-Trichloroethyl)Carbamates. An Analysis of the Link Between Structure and Pesticide Activity**

927M0178B St. Petersburg ZHURNAL OBSHCHEY  
KHIMII in Russian Vol 61 (123) No 12, Dec 91  
(manuscript received 11 Jul 90) pp 2672-2679

[Article by R.I. Tarasova, V.V. Moskva, N.I. Sinitsina, L.A. Vasyakina, I.Z. Batyrshin, V.R. Pekurovskiy, and



N.V. Tarabukin, Kazan Chemical Technology Institute  
imeni S.M. Kirov; UDC 547.468+495.1]

[Abstract] The link between the structure and pesticide activity of a series of phosphorylmethyl-N-(1-hydroxy-2,2,2-trichloroethyl)carbamates was examined. A mixture of 0.1 mole phosphorylated carbamate and 0.3 mole chloral was heated in a water bath for 2 to 2.5 hours. The excess chloral was removed in a vacuum at 80°C, and 10 to 20 ml aqueous alcohol (1:1) was added to the residue. The mixture was heated until the alcohol dissolved and was left to crystallize. The crystals were filtered off, rinsed with water, and dried. The resultant phosphorylmethyl-N-(1-hydroxy-2,2,2-trichloroethyl)carbamates were then subjected to a series of studies to determine their pesticide activity. A WP-80 spectrometer was used to record the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, and a UR-20 spectrometer operating in the frequency range from 400 to 3600  $\text{cm}^{-1}$  was used to

record the IR spectra. A Unified Series (YeS) computer was used along with a program written in Fortran and PL/1 to analyze the 87 study compounds with respect to four types of pesticide activity. The starting compounds were coded in the form of a vector, with different numerical codes used to designate each of the different substituents. The studies performed established that the degree to which pesticide activity is expressed depends on the spatial structure of the phosphoryl group and the electron acceptor properties of the substituent at the ether atom of the carbon. The strongest pesticide activity was detected in carbamates with bulk substituents ( $\text{C}_6\text{H}_5$ , iso- $\text{C}_3\text{H}_7\text{O}$ ). An analogous effect was observed in the case of carbamates with chlorine-substituted alkoxy groups at the phosphorus atom. The studies further indicated that adding a 1-hydroxy-2,2,2-trichloroethyl substituent to the nitrogen atom results in a significant increase in the growth-regulating activity of the study compounds. Tables 7; references 13 (Russian).

**Gas Chromatography on Methacrylate Polymers, Modified with Cobalt Cations**

927M0175H Moscow *ZHURNAL FIZICHESKOY KHIMII* in Russian Vol 66, No 4, Apr 92 (manuscript received 1 Mar 91) pp 1043-1048

[Article by N. P. Platonova, V. O. Ulogov, I. Gradil, and F. Shvets, Physical Chemistry Institute, Moscow; Macromolecular Chemistry Institute, Prague; UDC 543.544]

[Abstract] Development of the gas adsorption variant of chromatography is related to progress in new highly selective adsorbents. This has drawn interest to macroporous polymers which make it possible to easily control surface chemistry. The great variety of available polymers having functional groups includes polycomplexonates, i.e. complexes of ionites and metal ions such as transition metals. Polymers, modified with metal ions are being studied as potential column fillers, although systematic investigation has only just begun. In the present work a study was made of the gas chromatographic properties of aminated 2,3-epoxypropylmethacrylate ethylenedimethacrylate copolymer modified with a solution of  $\text{Co}(\text{NO}_3)_2$ . It was demonstrated that preliminary heating of the sample results in removal of water from the coordination shell of the cation thereby increasing the retention of adsorbing molecules. The nature of the functional group in the adsorbing molecule affects not only the energy magnitude of the specific interaction, but also the energy of its non-specific interaction with the surface. Adsorption is greatly enhanced by the orientational interaction of the cobalt-containing polymer with the surface. Figures 5, references 5: 2 Russian, 3 Western.

**Polynuclear Rhodium (III) Complexes With Nitrite Ions**

927M0188D Moscow *KOORDINATSIONNAYA KHIMIYA* in Russian Vol 18 No 1, Jan 92 (manuscript received 21 May 90, after final revision 12 Jul 91) pp 93-99

[Article by S. P. Khrenenko, A. V. Belyayev, V. N. Mitkin, Institute of Inorganic Chemistry, Siberian Department, USSR Academy of Sciences; UDC 546.97.131-141]

[Abstract] An attempt was made to synthesize polynuclear rhodium (III) complexes using thermal breakdown of metal hexanitrite salts which, along with the nitrite ions contained also  $\text{NH}_4^+$  ions. The latter facilitated the oxidation-reduction interaction of the ligands with external cations and promoted removal of the product into the gaseous phase. Specifically, products of thermal breakdown of  $(\text{NH}_4)_2\text{Na}[\text{Rh}(\text{NO}_2)_6]$  (I) obtained in the range of 120-300° were investigated. Both closed and

open systems were used; the products were characterized by chemical analysis, ESR, IR, NMR spectroscopy and by x-ray phase analysis. It was shown that thermal breakdown of (I) was accompanied by splitting of the ammonium ion and nitrous acid which then converted to  $\text{NO}_2$ ,  $\text{NO}$  and water. The final product obtained in 68-70% yield was a yellow powder soluble in water, alcohol and acetone. It was stable on prolonged storage. Both the open and closed reactions yielded polynuclear rhodium compounds  $\text{Na}_2[\text{Ph}_2(\text{NO}_2)_6(\text{OH})_2(\text{H}_2\text{O})_2]$  and  $\text{Na}_4[\text{Ph}_4(\text{NO}_2)_8(\text{OH})_8(\text{H}_2\text{O})_2]$ . The critical temperature for the polymerization was 282° above which the macromolecules began to break down. Table 1; figures 2; references 11: 7 Russian (1 by Western author), 4 Western.

**Diffusionphoresis During Formation of Polymer Coatings**

927M0191C Kiev *UKRAINSKIY KHIMICHESKIY ZHURNAL* in Russian Vol 58, No 5, May 92 (manuscript received 4 Jul 89, after revision 27 Jul 90) pp 390-396

[Article by Z. R. Ulberg, N. N. Ivzhenko, G. L. Dvornichenko, R. O. Buadze, and S. A. Koniashvili, Physical Chemistry Institute, Kiev; Electronic-Ionic Technology SRI, Tbilisi; UDC 667.647.22:678.041.6]

[Abstract] Significant successes in the field of electronic-surface phenomena paved the way for the development of new processes in forming composite polymeric coatings, such as diffusionphoresis, i.e. the movement of particles across an electrolyte concentration gradient. The process of diffusionphoretic coating includes two stages: a movement of particles toward a surface, and the concentration and coagulation of these particles at an electrode to form a deposit. The electrolyte concentration gradient is formed as a result of redox reactions taking place on the surface of a metallic substrate. Advantages of this technology, as compared to electrophoresis, include of high process efficiency, the ability to apply coatings to both conducting and non-conducting surfaces, and the use of ecologically clean solutions and dispersions, as well as low cost. Diffusionphoretic coatings also have high physical-mechanical and electrical properties. In the present work a study was made of the rules governing the formation of composite diffusionphoretic coatings using organic (polymeric) and inorganic dispersions and their properties. It was established that formation of such deposits include the diffusionphoretic transport of particles to a substrate resulting in their concentration. Deposition may be controlled by altering the concentration of the dispersed phase, its composition, pH value, and duration of the process. Figures 5; references 9: 7 Russian, 2 Western.

**Evaluation of Relative Biological Availability of Cesium-137 in Fallout and In Its Total Biological Availability in Soils on Territories, Subjected to Radioactive Contamination**

927M0192 Moscow AGROKHIMIYA in Russian No 2, Feb 92 (manuscript received 4 Jun 91) pp 102-110

[Article by P. F. Bondar, Yu. A. Ivanov, and A. G. Ozornov, Agricultural Radiobiology SRI, Kiev; UDC 632.118.3:546.36:631.811]

[Abstract] Features governing the migration of artificial radionuclides in the soil-plant chain are normally studied using water-soluble radioisotopes. As a result of the interaction of any given radionuclide with a soil, its availability to plants is decreased and is determined by the physical-chemical properties of the soil. Methods for predicting expected levels of plant contamination in various soils are developed from data on the accumulation of radionuclides in plants in respect to the agrochemical properties of the soil. When a territory is

contaminated with radionuclides having unknown physical-chemical forms and unknown distribution throughout the area, it is impossible to dependably predict the contamination of crops grown on this area. Thus resolving the problem of evaluating the differences in availability of radionuclides to plants in various parts of a territory on the basis of physical-chemical properties of the fallout in comparison to the availability of radionuclides introduced to the soil in water-soluble form, is urgent. In the present work a method for comparative evaluation of biologically available radionuclides in fallout relative to their availability in water-soluble form is presented. It is demonstrated that beyond the 30 km limits of the Chernobyl Nuclear Power Plant, the availability of Ce-137 in fallout is comparable to the availability of radionuclides introduced to the soil in water-soluble form. Under the soil conditions of the Ukrainian polessie, the variability of Ce-137 accumulation in crops is determined by the basic overall biological availability of the radionuclide in the soil. Figure 1; references 11 (Russian).

**Promoting Action of Silver in Ethylene Hydrogenation Reactions on Nickel Films**

927M0175J Moscow *ZHURNAL FIZICHESKOY KHIMII in Russian* Vol 66, No 4, Apr 92 (manuscript received 12 Dec 91) pp 1125-1129

[Article by L. M. Kuzhel, I. I. Mikhalenko, and V. D. Yagodovskiy, Friendship of Peoples Univerity imeni Patrice Mumumba; UDC 541.128]

[Abstract] Binary systems of active and inactive metals are of special interest in connection with the study of the structure and electronic properties of bimetallic systems

and their adsorption and catalytic activities. Previously, only systems having unlimited solubility of one metal in another in the form of carried catalysts were studied. In the present work a study was made of the hydrogenation of ethylene over films of nickel modified with various amounts of silver at 276-333 K. Coating the nickel surface with silver accelerated the velocity of ethylene hydrogenation in comparison to nickel foil alone. The increased activity of the catalyst is evidently due to the increase in adsorption potential of the nickel surface in the vicinity of silver particles. Figures 2; references 9: 6 Russian, 3 Western.



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30 Nov 1992